

D E C L A R A T I O N

I, SHINICHI USUI, a Japanese Patent Attorney registered No.9694, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No.2002-310250 filed on October 24, 2002 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 30th day of April, 2008

A handwritten signature in black ink, appearing to read 'Shinichi Usui', is written over a horizontal line.

SHINICHI USUI

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy
of the following application as filed with this office.

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Application Number: Japanese Patent Application
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Applicant(s): CANON KABUSHIKI KAISHA

November 27, 2003

Commissioner,
Patent Office

Yasuo IMAI

(Seal)

Certificate No. 2003-3097900

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Identification No. [000001007]

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(Reason of Change) New Registration

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2002-310250

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[Reference No.] 4771087

[Date] October 24, 2002

[Addressed to] Commissioner of the
Patent Office

[International Classification] C12P 7/62
C08G 63/06

[Title of the Invention] NOVEL POLYHYDROXY ALKANOATE
COPOLYMER INCLUDING WITHIN MOLECULE
UNIT HAVING VINYL GROUP OR CARBOXYL
GROUP IN SIDE CHAIN, AND PRODUCING
METHOD THEREFOR

[Number of the Claims] 35

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[Amount]	¥21,000
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[Material]	Specification 1
[Material]	Drawings 1
[Material]	Abstract 1
[Proof requirement]	necessary

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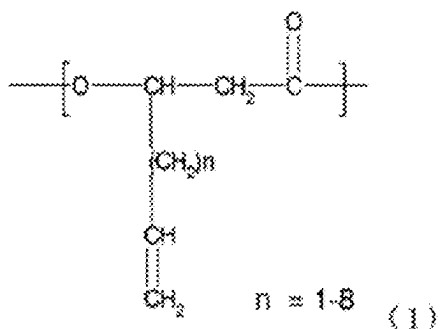
[Name of the Document] Specification

[Title of the Invention] Novel Polyhydroxy Alkanoate
Copolymer including within Molecule Unit Having Vinyl
5 Group or Carboxyl Group in Side Chain, and Producing
Method Therefor

[Claim(s)]

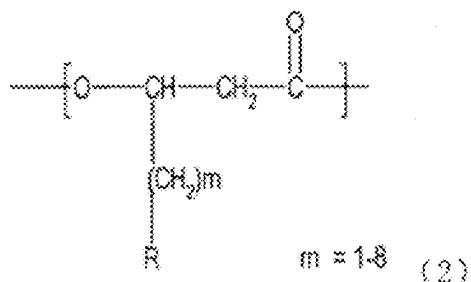
[Claim 1] A polyhydroxy alkanoate copolymer
characterized in including at least a 3-hydroxy- ω -
10 alkenoic acid unit represented by a chemical formula
(1) in a molecule, and simultaneously at least a 3-
hydroxy- ω -alkanoic acid unit represented by a chemical
formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid
unit represented by a chemical formula (3) in the
15 molecule:

[Chemical Formula 1]



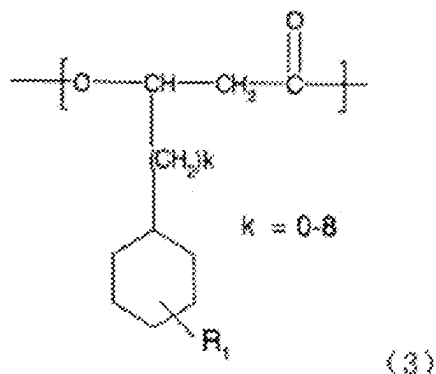
in which n represents an integer selected within a
range indicated in the chemical formula; and in case
20 plural units are present, n may be the same or
different for each unit;

[Chemical Formula 2]



in which m represents an integer selected within a range indicated in the chemical formula; R represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit;

[Chemical Formula 3]

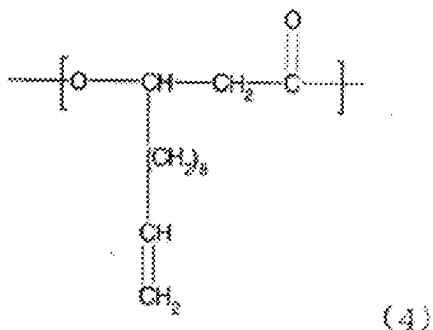


in which R₁ being a substituent on a cyclohexyl group represents a hydrogen atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R₁ and k may be the same or different for each unit.

[Claim 2] The polyhydroxy alkanoate copolymer

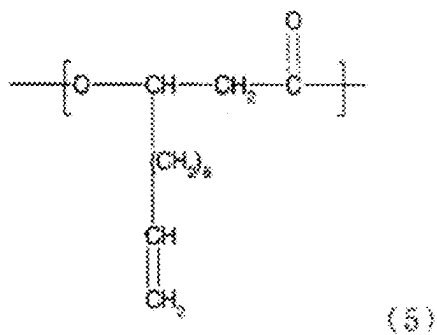
according to claim 1, wherein the 3-hydroxy- ω -alkenoic acid unit represented by the chemical formula (1) is any one of a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

5 [Chemical Formula 4]



a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

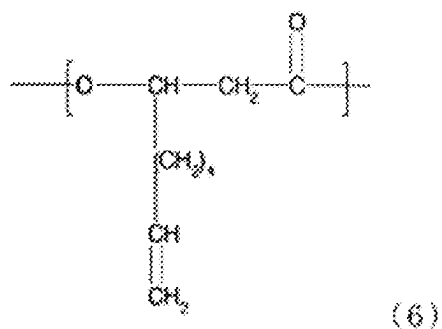
[Chemical Formula 5]



10

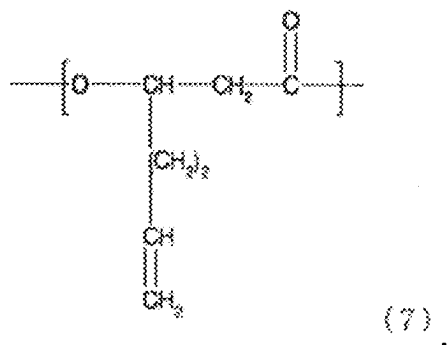
a 3-hydroxy-8-nonenic acid unit represented by a chemical formula (6): and

[Chemical Formula 6]



a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7)

[Chemical Formula 7]

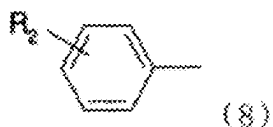


5

[Claim 3] The polyhydroxy alkanoate copolymer according to claim 1 or 2, wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from the group consisting of chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (8):

[Chemical Formula 8]

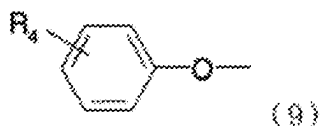


15 represents a group of non-substituted or substituted

phenyl groups in which R_2 , a substituent on an aromatic ring and represents an H atom, represents a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a COOR_3 group (R_3 represents an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

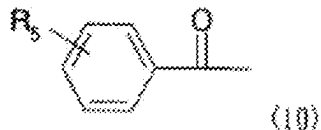
[Chemical Formula 9]



represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 10]



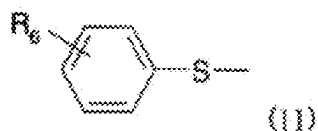
represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on

an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and in case plural units are present, R₅ may be the

5 same or different for each unit;

the chemical formula (11)

[Chemical Formula 11]



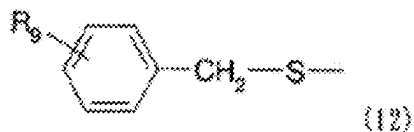
represents a group of substituted or non-substituted

10 phenylsulfanyl groups in which R₆ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₇ group, a SO₂R₈ group (R₇ represents either one of H, Na, K, CH₃ and C₂H₅; and R₈ represents either one of OH, ONa,

15 OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₆ may be the same or different for each unit;

the chemical formula (12):

20 [Chemical Formula 12]



represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R₉ represents a

substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀ group, a SO₂R₁₁ group (R₁₀ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₁ represents either one of OH, 5 ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₉ may be the same or different for each unit;

the chemical formula (13):

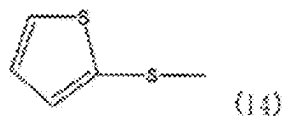
10 [Chemical Formula 13]



represents a 2-thienyl group;

the chemical formula (14)

[Chemical Formula 14]

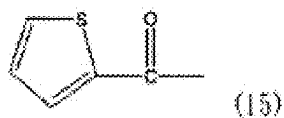


15

represents a 2-thienylsulfanyl group;

the chemical formula (15):

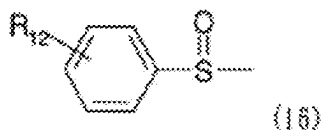
[Chemical Formula 15]



20 represents a 2-thienylcarbonyl group;

the chemical formula (16):

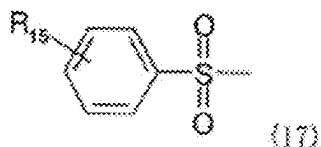
[Chemical Formula 16]



represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

[Chemical Formula 17]

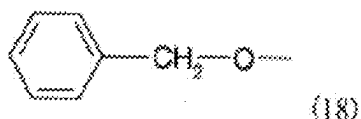


represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_{17} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_{15} may be

the same or different for each unit; and

the chemical formula (18):

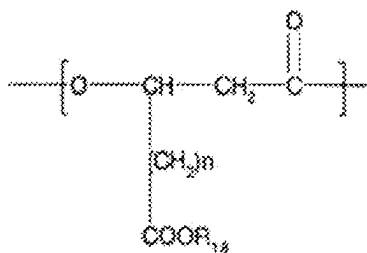
[Chemical Formula 18]



5 represents a (phenylmethyl)oxy group.

[Claim 4] A polyhydroxy alkanooate copolymer characterized in including at least a 3-hydroxy- ω -carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least
 10 a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

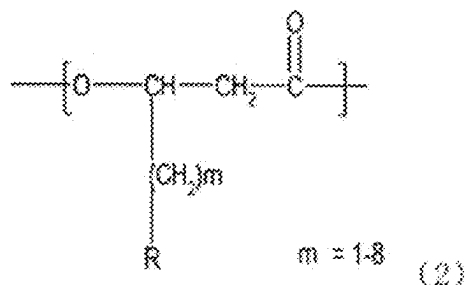
[Chemical Formula 19]



$n = 1-8 \quad (19)$

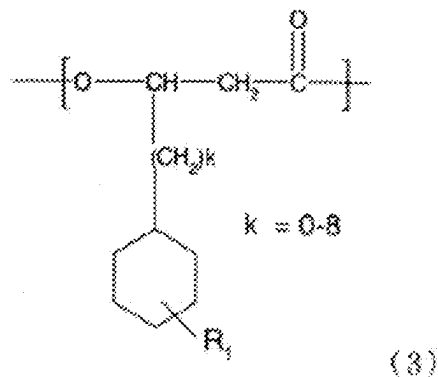
15 in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom or a K atom: and in case plural units are present, n and R_{18} may be the same or
 20 different for each unit;

[Chemical Formula 20]



in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit; and

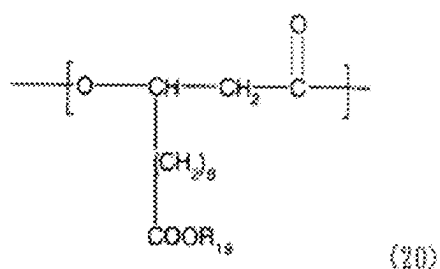
[Chemical Formula 21]



in which R₁ represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R₁ and k may be the same or different for each unit.

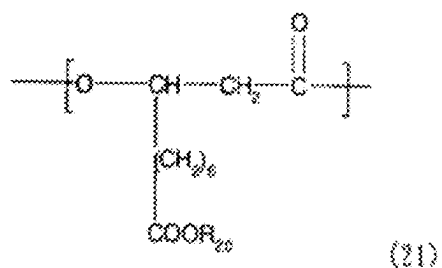
[Claim 5] The polyhydroxy alkanoate copolymer according to claim 4, wherein the 3-hydroxy- ω -carboxyalkanoic acid unit represented by the chemical formula (19) is any one of a 3-hydroxy-11-
5 carbonylundecanoic acid unit represented by a chemical formula (20):

[Chemical Formula 22]



(R₁₉ represents an H atom, a Na atom or a K atom; and
10 in case plural units are present, R₁₉ may be the same or different for each unit),
a 3-hydroxy-9-carboxynonanoic acid unit represented by a chemical formula (21):

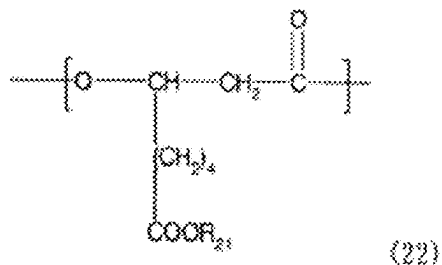
[Chemical Formula 23]



15 (R₂₀ represents an H atom, a Na atom or a K atom and in case plural units are present; and R₂₀ may be the same or different for each unit),

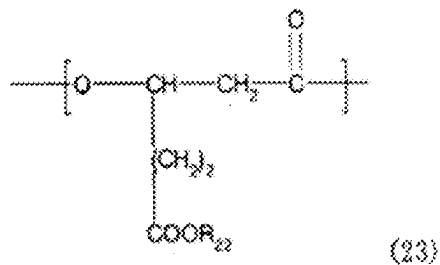
a 3-hydroxy-7-carboxyheptanoic acid unit represented by a chemical formula (22):

[Chemical Formula 24]



- 5 (R₂₁ represents an H atom, a Na atom or a K atom; and in case plural units are present, R₂₁ may be the same or different for each unit), and a 3-hydroxy-5-carboxyvaleric acid unit represented by a chemical formula (23):

10 [Chemical Formula 25]



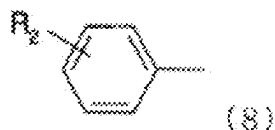
(R₂₂ represents an H atom, a Na atom or a K atom; and in case plural units are present, R₂₂ may be the same or different for each unit).

- 15 [Claim 6] The polyhydroxy alkanoate copolymer according to claim 4 or 5, wherein R in the chemical formula (2), represents a residue having a phenyl structure or a thienyl structure selected from chemical formulas (8), (9), (10), (11), (12), (13), (14), (15),

(16), (17), and (18):

the chemical formula (8):

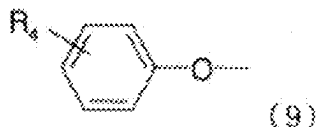
[Chemical Formula 26]



5 represents a group of non-substituted or substituted phenyl groups in which R_2 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a COOR_3 group (R_3
10 representing an H atom, a Na atom or a K atom), a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_2 may be the same or different for each unit;

the chemical formula (9):

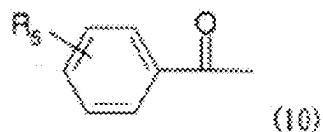
15 [Chemical Formula 27]



represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
20 a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 28]



represents a group of non-substituted or substituted
5 benzoyl groups in which R_5 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;
and in case plural units are present, R_5 may be the
10 same or different for each unit;

the chemical formula (11):

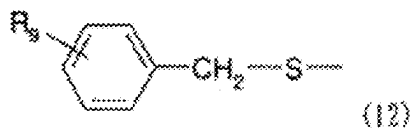
[Chemical Formula 29]



represents a group of substituted or non-substituted
15 phenylsulfanyl groups in which R_6 represents a
substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$
group, a SO_2R_8 group (R_7 represents either one of H, Na,
K, CH_3 and C_2H_5 ; and R_8 represents either one of OH, ONa,
20 OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5
group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$
group; and in case plural units are present, R_6 may be
the same or different for each unit;

the chemical formula (12):

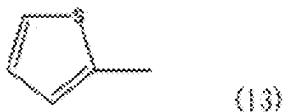
[Chemical Formula 30]



represents a group of substituted or non-substituted
 5 (phenylmethyl)sulfanyl groups in which R₉ represents a
 substituent on an aromatic ring and represents an H
 atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀
 group, a SO₂R₁₁ group (R₁₀ represents either one of H,
 Na, K, CH₃ and C₂H₅; and R₁₁ represents either one of OH,
 10 ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C
 group; and in case plural units are present, R₉ may be
 the same or different for each unit;

the chemical formula (13):

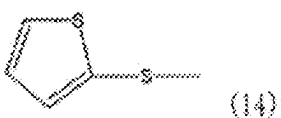
15 [Chemical Formula 31]



represents a 2-thienyl group;

the chemical formula (14):

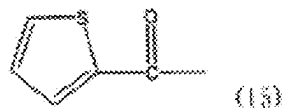
[Chemical Formula 32]



20 represents a 2-thienylsulfanyl group;

the chemical formula (15):

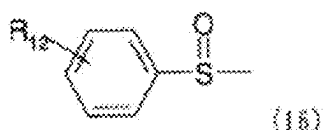
[Chemical Formula 33]



represents a 2-thienylcarbonyl group;

the chemical formula (16):

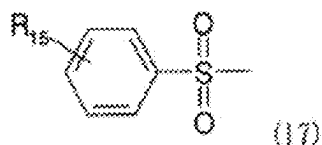
5 [Chemical Formula 34]



represents a group of substituted or non-substituted
phenylsulfinyl groups in which R_{12} represents a
substituent on an aromatic ring and represents an H
10 atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$
group, a SO_2R_{14} group (R_{13} represents either one of H,
Na, K, CH_3 and C_2H_5 ; and R_{14} represents either one of OH,
ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a
 C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$
15 group; and in case plural units are present, R_{12} may be
the same or different for each unit;

the chemical formula (17):

[Chemical Formula 35]

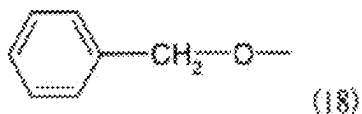


20 represents a group of substituted or non-substituted
phenylsulfonyl groups in which R_{15} represents a
substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆ group, a SO₂R₁₇ group (R₁₆ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₇ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
5 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₅ may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 36]



10

represents a (phenylmethyl)oxy group.

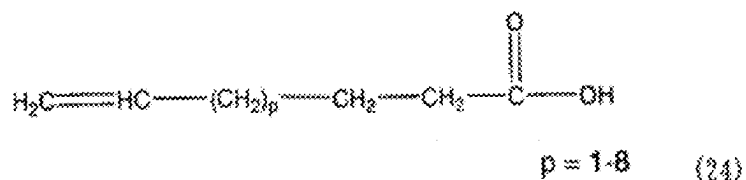
[Claim 7] The polyhydroxy alkanoate copolymer according to any one of claims 1 to 6, wherein a number-averaged molecular weight is within a range from
15 1000 to 1000000.

[Claim 8] A method for producing a polyhydroxy alkanoate copolymer characterized in including a biosynthesis by a microorganism having an ability of producing a polyhydroxy alkanoate copolymer including
20 at least a 3-hydroxy- ω -alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a
25 chemical formula (3) in the molecule, from at least an

ω -alkenoic acid represented by a chemical formula (24)
and at least a compound represented by a chemical
formula (25) or at least an ω -cyclohexylalkanoic acid
represented by a chemical formula (26) as starting

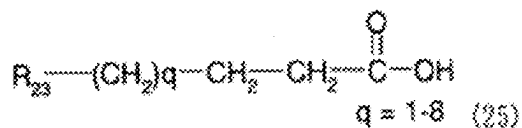
5 materials:

[Chemical Formula 37]



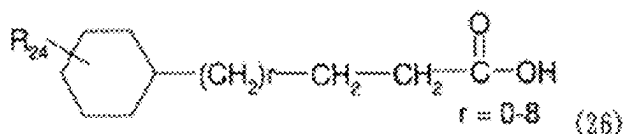
in which p represents an integer selected within a
range indicated in the chemical formula;

10 [Chemical Formula 38]



in which q represents an integer selected within a
range indicated in the chemical formula; and R_{23}
includes a residue having a phenyl structure or a
15 thienyl structure;

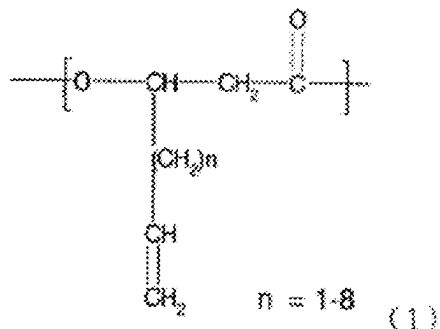
[Chemical Formula 39]



in which R_{24} represents a substituent on a cyclohexyl
group and represents an H atom, a CN group, a NO_2 group,
20 a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group,

a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r represents an integer selected within a range indicated in the chemical formula;

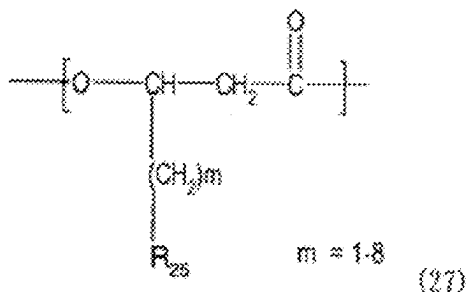
[Chemical Formula 40]



5

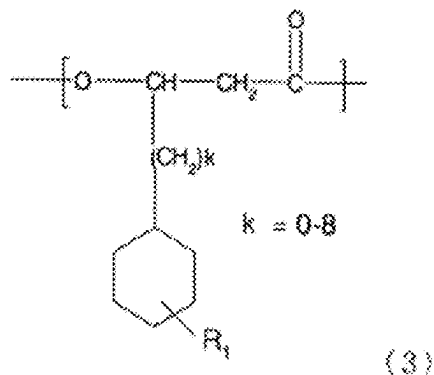
in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

10 [Chemical Formula 41]



15 in which m represents an integer selected within a range indicated in the chemical formula; R_{25} represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R_{25} may be the same or different for each unit; and

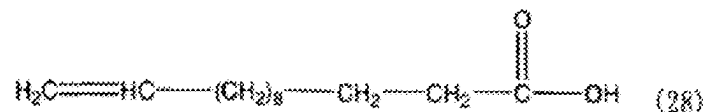
[Chemical Formula 42]



in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

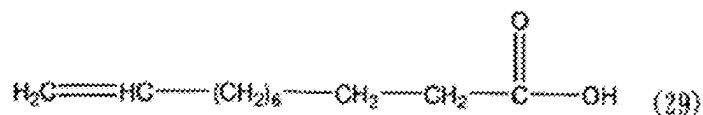
[Claim 9] The method for producing a polyhydroxy alkananoate copolymer according to claim 8, wherein the ω -alkenoic acid represented by the chemical formula (24) is a 12-tridecenoic acid represented by a chemical formula (28): or

[Chemical Formula 43]



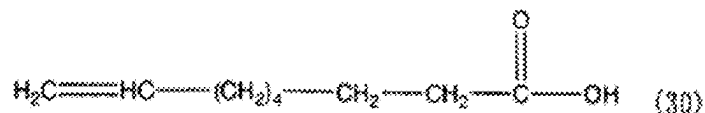
a 10-undecenoic acid represented by a chemical formula (29): or

[Chemical Formula 44]



a 8-nonenoic acid unit represented by a chemical formula (30):

[Chemical Formula 45]

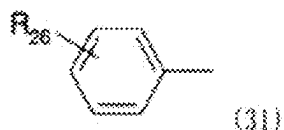


5

[Claim 10] The method for producing a polyhydroxy alkanooate copolymer according to claim 8 or 9, wherein R_{23} in the chemical formula (25) and R_{25} in the chemical formula (27), each represents a residue having a phenyl structure or a thienyl structure, are selected from chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (31):

[Chemical formula 46]



15

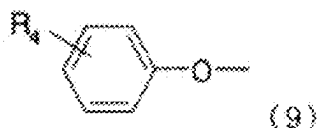
represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and in case plural units are present,

20

R₂₆ may be the same or different for each unit;

the chemical formula (9):

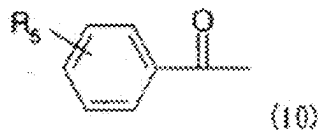
[Chemical Formula 47]



- 5 represents a group of non-substituted or substituted phenoxy groups in which R₄ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a SCH₃ group, a CF₃ group, a C₂F₅ group, or
10 a C₃F₇ group; and in case plural units are present, R₄ may be the same or different for each unit;

the chemical formula (10):

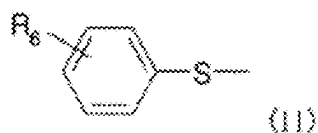
[Chemical Formula 48]



- 15 represents a group of non-substituted or substituted benzoyl groups in which R₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group;
20 and in case plural units are present, R₅ may be the same or different for each unit;

the chemical formula (11):

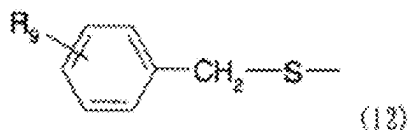
[Chemical Formula 49]



represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 50]



represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present,

R₉ may be the same or different for each unit;

the chemical formula (13):

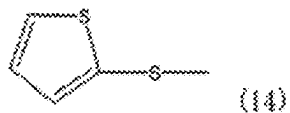
[Chemical Formula 51]



5 represents a 2-thienyl group;

the chemical formula (14):

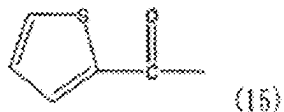
[Chemical Formula 52]



represents a 2-thienylsulfanyl group;

10 the chemical formula (15):

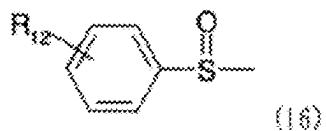
[Chemical Formula 53]



represents a 2-thienylcarbonyl group;

the chemical formula (16):

15 [Chemical Formula 54]



represents a group of substituted or non-substituted

phenylsulfinyl groups in which R₁₂ represents a

substituent on an aromatic ring and represents an H

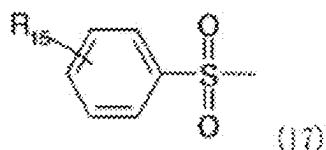
20 atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₃

group, a SO₂R₁₄ group (R₁₃ representing either one of H,

Na, K, CH₃ and C₂H₅; and R₁₄ representing either one of
 OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃
 group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a
 (CH₃)₃-C group; and in case plural units are present,
 5 R₁₂ may be the same or different for each unit;

the chemical formula (17):

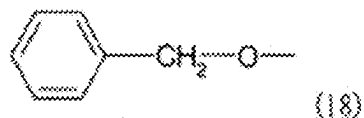
[Chemical Formula 55]



represents a group of substituted or non-substituted
 10 phenylsulfonyl groups in which R₁₅ represents a
 substituent on an aromatic ring and represents an H
 atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆
 group, a SO₂R₁₇ group (R₁₆ representing either one of H,
 Na, K, CH₃ and C₂H₅; and R₁₇ representing either one of
 15 OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃
 group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a
 (CH₃)₃-C group; and in case plural units are present,
 R₁₅ may be the same or different for each unit; and

the chemical formula (18):

20 [Chemical Formula 56]



represents a (phenylmethyl)oxy group.

[Claim 11] The method for producing a polyhydroxy

alkanoate copolymer according to any one of claims 8 to 10, wherein said microorganism is cultured in a culture medium including at least a ω -alkenoic acid represented by the chemical formula (24) and at least a compound
5 represented by the chemical formula (25) or at least a ω -cyclohexylalkanoic acid represented by the chemical formula (26).

[Claim 12] The method for producing a polyhydroxy alkanoate copolymer according to claim 11, wherein said
10 microorganism is cultured in a culture medium including, in addition to at least an ω -alkenoic acid represented by the chemical formula (24) and at least a compound represented by the chemical formula (25) or at least a ω -cyclohexylalkanoic acid represented by the chemical
15 formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar, a linear alkanoic acid with 4 to 12 carbon atoms or a salt thereof.

[Claim 13] The method for producing a polyhydroxy
20 alkanoate copolymer according to claim 12, wherein for culturing said organism, the peptide to be added to the culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of piruvic acid,
25 oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof; amino acid or salt

thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid, aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected
5 from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[Claim 14] The method for producing a polyhydroxy
10 alkanolate copolymer according to any one of claims 8 to 13, characterized in including a step of culturing said microorganism in a culture medium including at least an ω -alkenoic acid represented by the chemical formula (24) and at least a compound represented by the
15 chemical formula (25) or at least an ω -cyclohexylalkanoic acid represented by the chemical formula (26), and recovering a polyhydroxy alkanolate copolymer including simultaneously at least a 3-hydroxy- ω -alkenoic acid unit represented by the
20 chemical formula (1) and a 3-hydroxy- ω -alkanoic acid unit represented by the chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by said microorganism, from cells of the microorganism.

25 [Claim 15] The method for producing a polyhydroxy alkanolate copolymer according to any one of claims 8 to 14, wherein said microorganism is a microorganism

belonging to *Pseudomonas* genus.

[Claim 16] The method for producing a polyhydroxy
alkanoate copolymer according to claim 15, wherein said
microorganism is at least one of *Pseudomonas cichorii*
5 YN2 strain (FERM BP-7375), *Pseudomonas cichorii* H45
strain (FERM BP-7374), *Pseudomonas jessenii* P161 (FERM
BP-7376) and *Pseudomonas putida* P91 (FERM BP-7373).

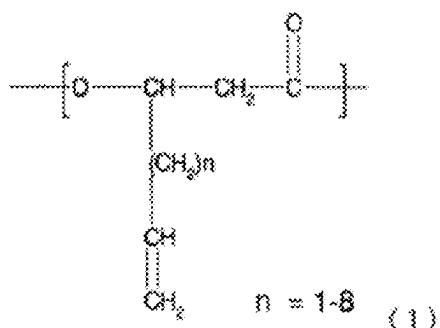
[Claim 17] A method for producing a polyhydroxy
alkanoate copolymer including at least a 3-hydroxy- ω -
10 carboxyalkanoic acid unit represented by a chemical
formula (19) in a molecule, and simultaneously at least
a 3-hydroxy- ω -alkanoic acid unit represented by a
chemical formula (2) or a 3-hydroxy- ω -
cyclohexylalkanoic acid unit represented by a chemical
15 formula (3) in the molecule comprising the steps of:
preparing a polyhydroxy alkanoate copolymer including
at least a 3-hydroxy- ω -alkenoic acid unit represented
by a chemical formula (1) in a molecule, and
simultaneously at least a 3-hydroxy- ω -alkanoic acid
20 unit represented by a chemical formula (2) or a 3-
hydroxy- ω -cyclohexylalkanoic acid unit represented by a
chemical formula (3) in the molecule as a starting
material, and

oxidizing and cleaving a double bond portion in
25 the polyhydroxy alkanoate represented in the chemical
formula (1) thereby

generating a polyhydroxy alkanoate copolymer

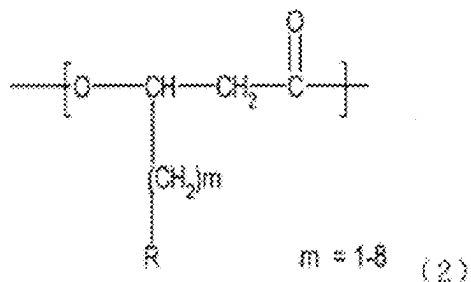
including at least a 3-hydroxy- ω -carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[Chemical Formula 57]



in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

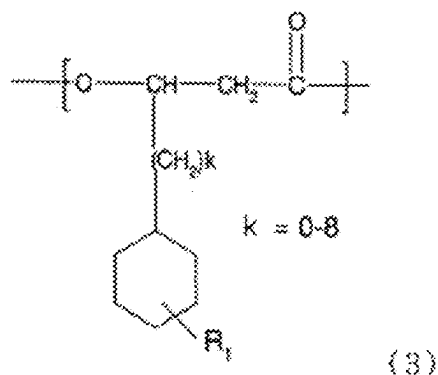
[Chemical Formula 58]



in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure and a thienyl

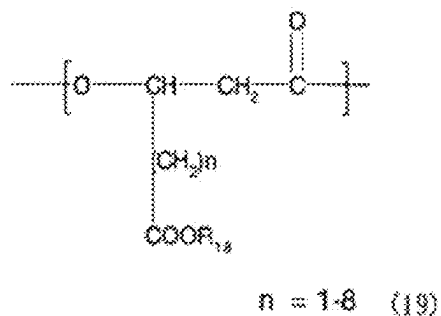
structure; and in case plural units are present, m and R may be the same or different for each unit;

[Chemical Formula 59]



- 5 in which R_1 represents a substituent on a cyclohexyl group selected from an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, and a C_3F_7 group; k represents an integer selected within a range indicated
- 10 in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit; and

[Chemical Formula 60]



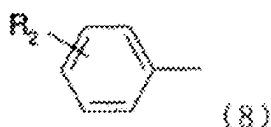
- 15 in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents

an H atom, a Na atom, or a K atom; and in case plural units are present, n and R₁₈ may be the same or different for each unit.

[Claim 18] The method for producing a polyhydroxy
5 alkanooate copolymer according to claim 17, wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

10 the chemical formula (8):

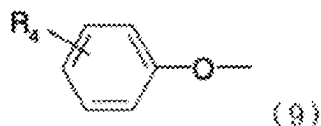
[Chemical Formula 61]



represents a group of non-substituted or substituted phenyl groups in which R₂ represents a substituent on
15 an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CH=CH₂ group, a COOR₃ group (R₃ representing an H atom, a Na atom or a K atom), a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and in case plural
20 units are present, R₂ may be the same or different for each unit;

the chemical formula (9):

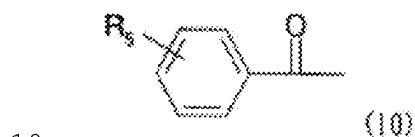
[Chemical Formula 62]



represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, 5 a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

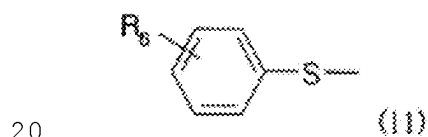
[Chemical Formula 63]



represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, 15 a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[Chemical Formula 64]

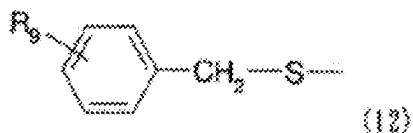


represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO₂ group, a COOR₇ group, a SO₂R₈ group (R₇ represents either one of H, Na, K, CH₃ and C₂H₅; and R₈ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₆ may be the same or different for each unit;

the chemical formula (12):

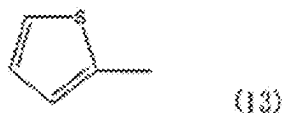
[Chemical Formula 65]



represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R₉ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀ group, a SO₂R₁₁ group (R₁₀ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₁ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₉ may be the same or different for each unit;

the chemical formula (13):

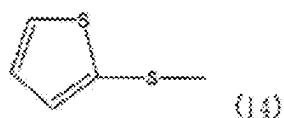
[Chemical Formula 66]



represents a 2-thienyl group;

the chemical formula (14):

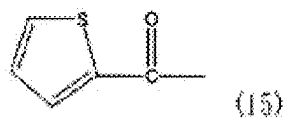
[Chemical Formula 67]



5 represents a 2-thienylsulfanyl group;

the chemical formula (15):

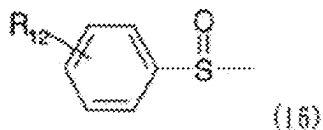
[Chemical Formula 68]



represents a 2-thienylcarbonyl group;

10 the chemical formula (16):

[Chemical Formula 69]



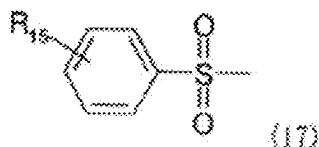
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_{12} represents a

15 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_{14} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3

20 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

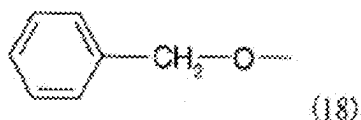
[Chemical Formula 70]



represents a group of substituted or non-substituted
 5 phenylsulfonyl groups in which R₁₅ represents a
 substituent on an aromatic ring and represents an H
 atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆
 group, a SO₂R₁₇ group (R₁₆ represents either one of H,
 Na, K, CH₃ and C₂H₅; and R₁₇ represents either one of OH,
 10 ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C
 group; and in case plural units are present, R₁₅ may be
 the same or different for each unit;

the chemical formula (18):

15 [Chemical Formula 71]

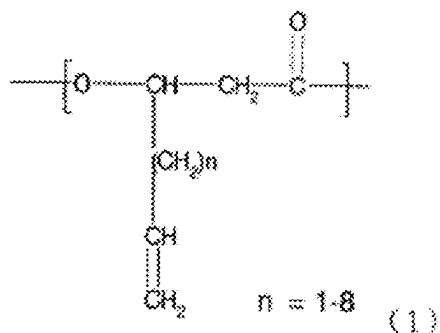


represents a (phenylmethyl)oxy group.

[Claim 19] The method according to claim 17 or 18,
 wherein said starting material polyhydroxy alkanoate
 20 copolymer including at least a 3-hydroxy- ω -alkenoic
 acid unit represented by a chemical formula (1) in a
 molecule, and simultaneously at least a 3-hydroxy- ω -
 alkanoic acid unit represented by a chemical formula

(27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, is produced by a method according to any one of claims 8 to 16;

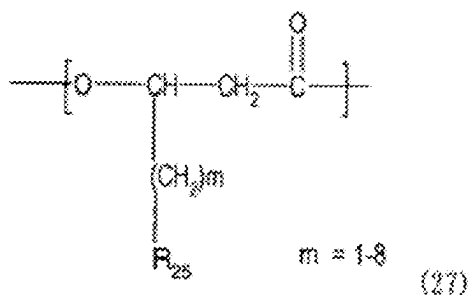
5 [Chemical Formula 72]



in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or

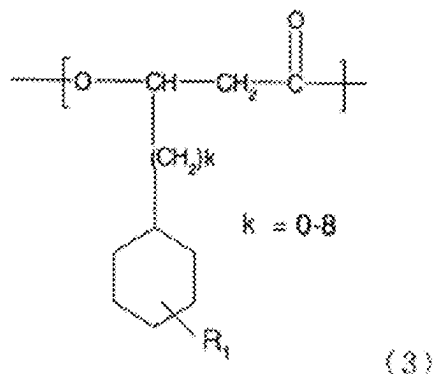
10 different for each unit;

[Chemical Formula 73]



in which m represents an integer selected within a range indicated in the chemical formula; R₂₅ represents
15 a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R₂₅ may be the same or different for each unit; and

[Chemical Formula 74]

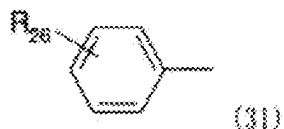


in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

[Claim 20] The method for producing a polyhydroxy alkanooate copolymer according to claim 19, wherein R_{25} in the chemical formula (27), representing a residue having a phenyl structure or a thienyl structure, is at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

the chemical formula (31):

[Chemical Formula 75]

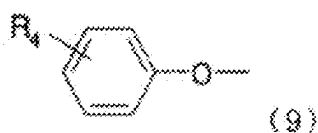


represents a group of substituted or non-substituted

phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a CF_3 group, a C_2F_5 group
5 or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

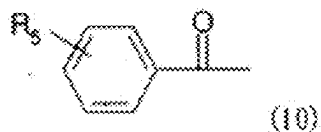
[Chemical Formula 76]



10 represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or
15 a C_3F_7 group; and in case plural units are present, R_4 may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 77]

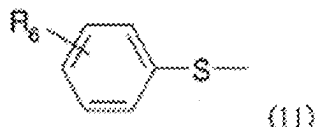


20 represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;

and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

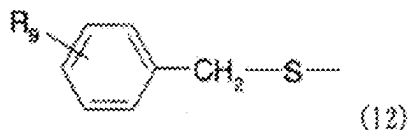
[Chemical Formula 78]



5 represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a COOR_7 group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[Chemical Formula 79]



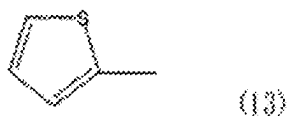
20 represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a COOR_{10} group, a SO_2R_{11} group (R_{10} representing either one of H,

Na, K, CH₃ and C₂H₅; and R₁₁ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H⁷ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present,

5 R9 may be the same or different for each unit;

the chemical formula (13):

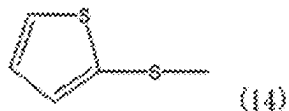
[Chemical Formula 80]



represents a 2-thienyl group;

10 the chemical formula (14):

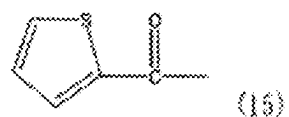
[Chemical Formula 81]



represents a 2-thienylsulfanyl group;

the chemical formula (15):

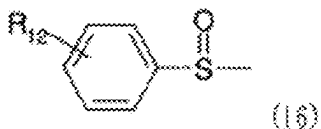
15 [Chemical Formula 82]



represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 83]



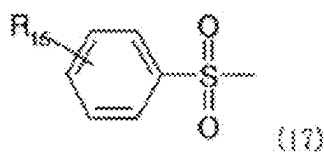
20

represents a group of substituted or non-substituted

phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_{12} may be the same or different for each unit;

the chemical formula (17):

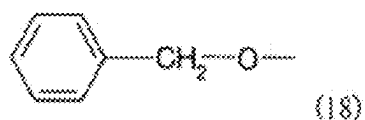
[Chemical Formula 84]



represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_{15} may be the same or different for each unit; and

the chemical formula (18):

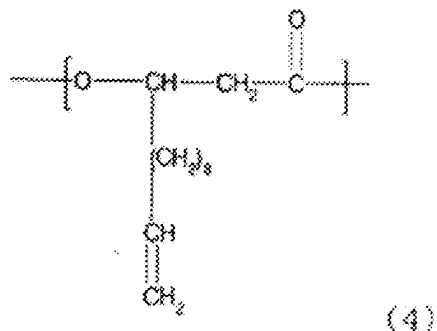
[Chemical Formula 85]



represents a (phenylmethyl)oxy group.

[Claim 21] The polyhydroxy alkanooate copolymer according to any one of claims 17 to 20, wherein the 3-hydroxy- ω -alkenoic acid unit represented by the chemical formula (1) is any one of a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

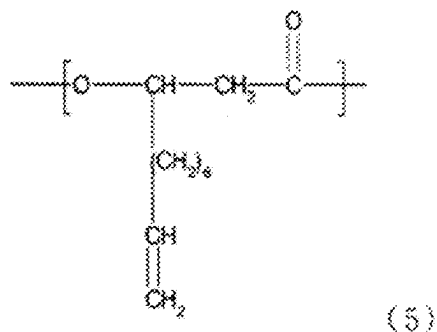
[Chemical Formula 86]



10

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

[Chemical Formula 87]

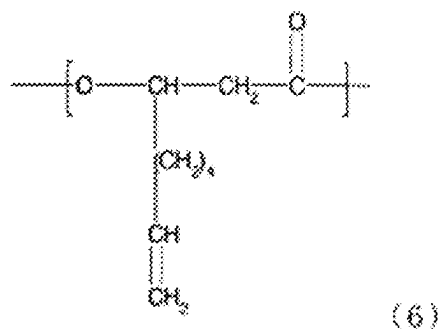


15

a 3-hydroxy-8-nonenic acid unit represented by a

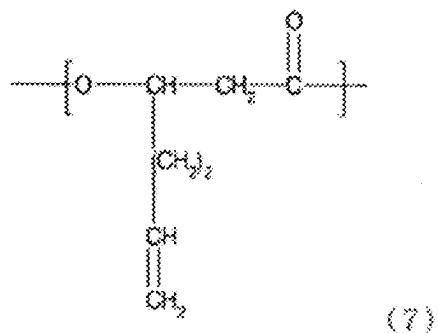
chemical formula (6): and

[Chemical Formula 88]



a 3-hydroxy-6-heptenoic acid unit represented by a
5 chemical formula (7)

[Chemical Formula 89]



[Claim 22] The producing method according to any
one of claims 17 to 21, wherein said oxidation and
10 cleavage reaction is carried out with an oxidant
selected from a group consisting of a permanganate, a
bichromate and a periodate.

[Claim 23] The producing method according to claim
22, wherein said oxidation and cleavage reaction is
15 carried out with a permanganate as an oxidant and under
an acidic condition.

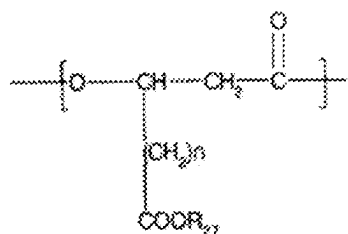
[Claim 24] The producing method according to any one of claims 17 to 21, wherein said oxidation and cleavage reaction is carried out with ozone.

[Claim 25] A method for producing a polyhydroxy
5 alkanooate copolymer, characterized in employing a polyhydroxy alkanooate copolymer including at least a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit represented by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid
10 unit represented by a chemical formula (27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule as a starting material,

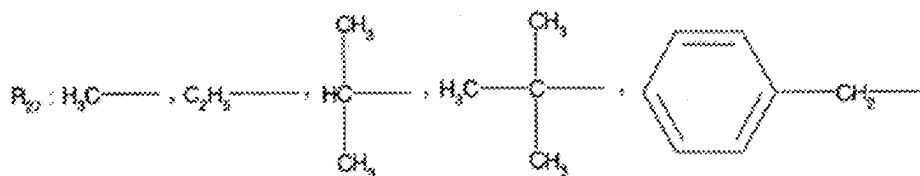
and executing a hydrolysis in the presence of an
15 acid or an alkali or executing a hydrogenolysis including a catalytic reduction,

thereby generating a polyhydroxy alkanooate copolymer including at least a 3-hydroxy- ω -carboxyalkanoic acid unit represented by a chemical
20 formula (19) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

25 [Chemical Formula 90]

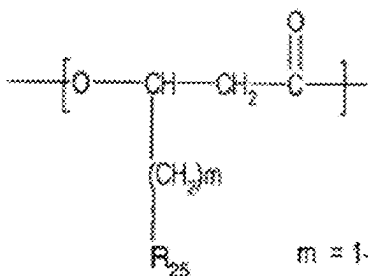


$n = 1-8$ (32)



in which n represents an integer selected within a
range indicated in the chemical formula; R₂₇ represents
any of residues indicated in the chemical formula; and
5 in case plural units are present, n and R₂₇ may be the
same or different for each unit;

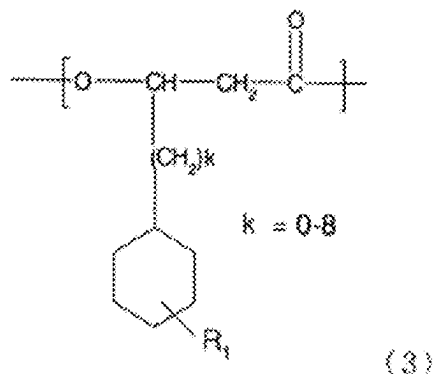
[Chemical Formula 91]



$m = 1-8$
(27)

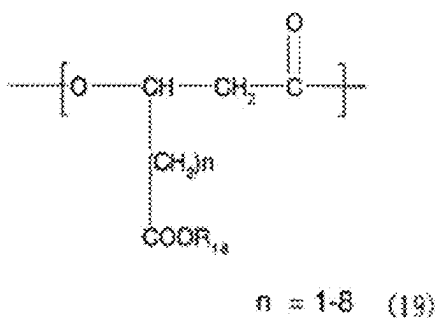
in which m represents an integer selected within a
10 range indicated in the chemical formula; R₂₅ includes a
residue having any of a phenyl structure and a thienyl
structure; and in case plural units are present, m and
R₂₅ may be the same or different for each unit;

[Chemical Formula 92]



in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit; and

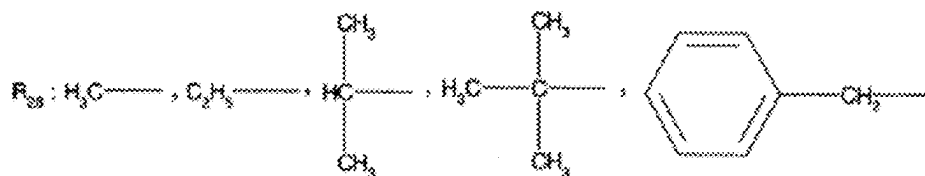
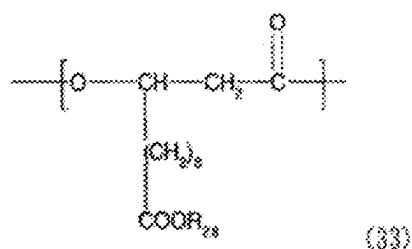
10 [Chemical Formula 93]



in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

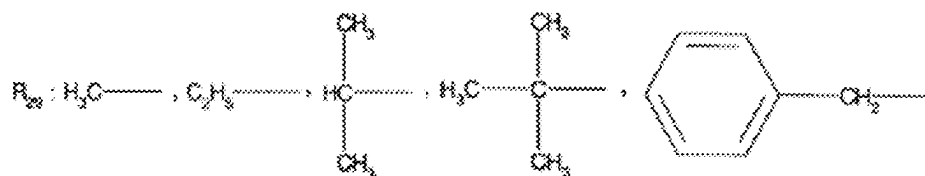
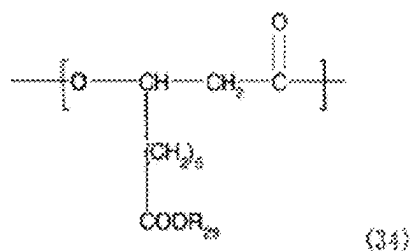
[Claim 26] The polyhydroxy alkanoate copolymer according to claim 25, wherein the 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) is any one of a 3-hydroxy-11-
 5 alkoxyundecanoic acid unit represented by a chemical formula (33):

[Chemical Formula 94]



(R₂₈ represents any of residues indicated in the
 10 chemical formula; and in case plural units are present,
 R₂₈ may be the same or different for each unit),
 a 3-hydroxy-9-alkoxycarboxynonanoic acid unit
 represented by a chemical formula (34):

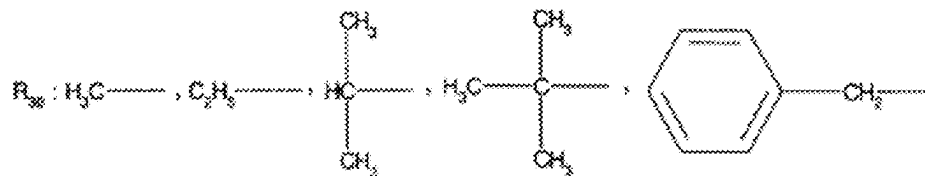
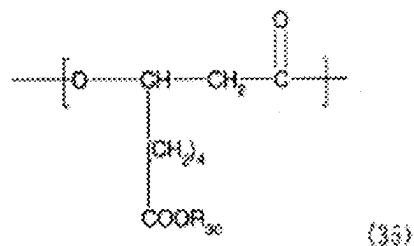
[Chemical Formula 95]



(R₂₉ represents any of residues indicated in the chemical formula; and in case plural units are present, R₂₉ may be the same or different for each unit),

- 5 a 3-hydroxy-7-alkoxycarboxyheptanoic acid unit represented by a chemical formula (35):

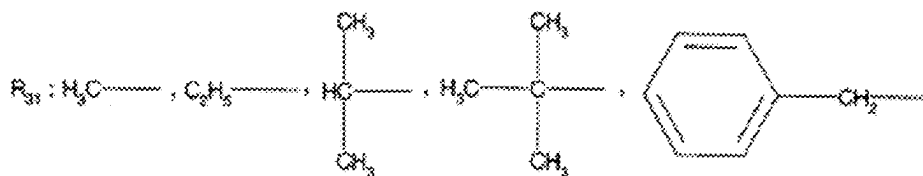
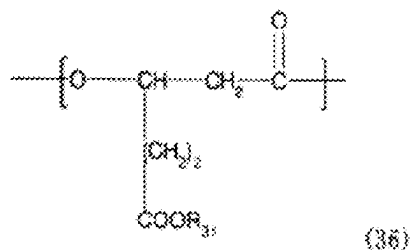
[Chemical Formula 96]



- (R₃₀ represents any of residues indicated in the chemical formula; and in case plural units are present, R₃₀ may be the same or different for each unit), and
- 10 a 3-hydroxy-5-alkoxycarboxyvaleric acid unit

represented by a chemical formula (36):

[Chemical Formula 97]

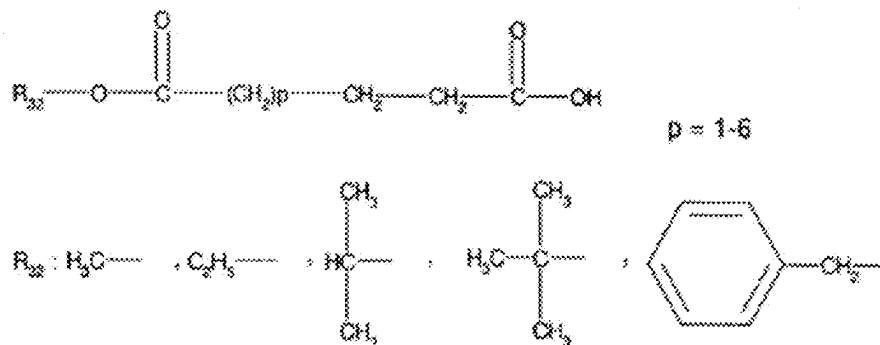


(R₃₁ represents any of residues indicated in the
 5 chemical formula; and in case plural units are present,
 R₃₁ may be the same or different for each unit).

[Claim 27] The method for producing a polyhydroxy
 alkanooate copolymer including the 3-hydroxy- ω -
 carboxyalkanoic acid according to claim 25 or 26 hydro-
 10 synthesized by a microorganism having an ability of
 producing a polyhydroxy alkanooate copolymer including
 at least a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit
 represented by a chemical formula (32) in a molecule,
 and simultaneously at least a 3-hydroxy- ω -alkanoic acid
 15 unit represented by a chemical formula (27) or a 3-
 hydroxy- ω -cyclohexylalkanoic acid unit represented by a
 chemical formula (3) in the molecule,

from a dicarboxylic acid monoester compound
 represented by a chemical formula (37):

[Chemical Formula 98]

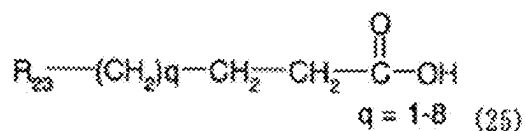


(37)

in which p represents an integer selected within a
 5 range indicated in the chemical formula; and R_{32}
 represents any of residues indicated in the chemical
 formula;

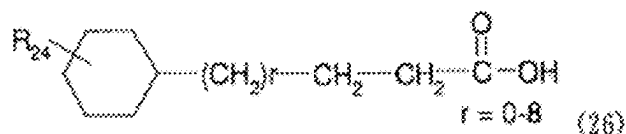
and at least a compound represented by a chemical
 formula (25) or at least a ω -cyclohexylalkanoic acid
 10 represented by a chemical formula (26) as starting
 materials:

[Chemical Formula 99]



in which q represents an integer selected within a
 15 range indicated in the chemical formula; and R_{23}
 includes a residue having a phenyl structure or a
 thienyl structure;

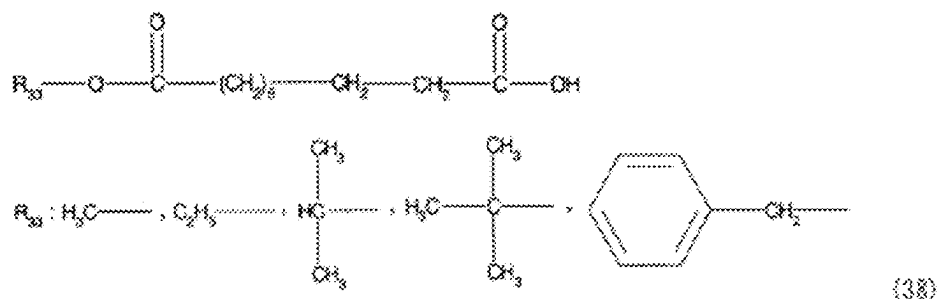
[Chemical Formula 100]



in which R₂₄ represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and r represents an integer selected within a range indicated in the chemical formula.

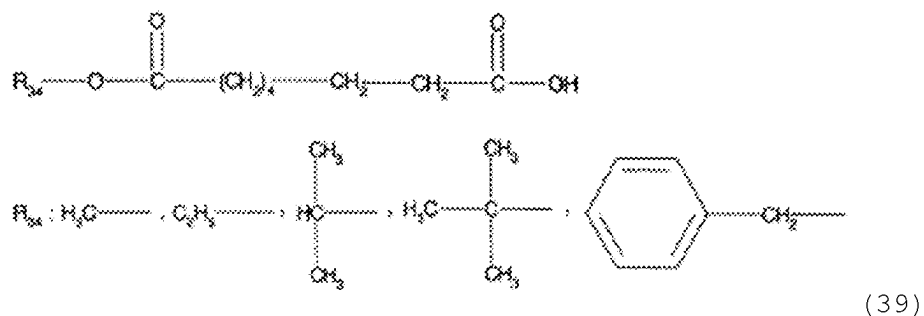
[Claim 28] The polyhydroxy alkanate copolymer according to claim 27, wherein the dicarboxylic acid monoester compound represented by the chemical formula (37) is any one of a sebacic acid monoester compound represented by a chemical formula (38):

[Chemical Formula 101]



(R₃₃ represents any of residues indicated in the chemical formula), or a suberic acid monoester compound represented by a chemical formula (39):

[Chemical Formula 102]

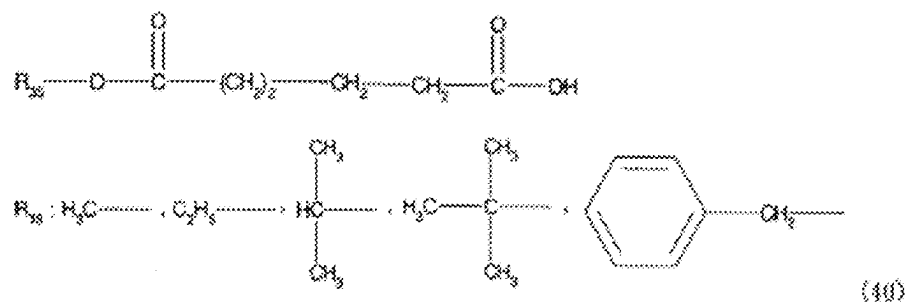


(R₃₄ represents any of residues indicated in the chemical formula), or

a adipic acid monoester compound represented by a

5 chemical formula (40):

[Chemical Formula 103]



(R₃₅ represents any of residues indicated in the chemical formula).

10 [Claim 29] The method for producing a polyhydroxy alkanooate copolymer including at least the 3-hydroxy- ω -carboxyalkanoic acid according to claim 27 or 28 in a molecule, which hydro-synthesizes a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit represented by the

15 chemical formula (32) by cultivating a microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by a chemical formula

(37), and at least a compound represented by the chemical formula (25) or at least a ω -cyclohexylalkanoic acid represented by a chemical formula (26).

5 [Claim 30] The method for producing a polyhydroxy alkanolate copolymer according to claim 29, wherein said microorganism is cultured in a culture medium including, in addition to at least a dicarboxylic acid monoester compound represented by the chemical formula (37), and
10 at least a compound represented by the chemical formula (25) or at least a ω -cyclohexylalkanoic acid represented by the chemical formula (26), at least one of a peptide, an yeast extract, an organic acid or a salt thereof, an amino acid or a salt thereof, a sugar,
15 a linear alkanolic acid with 4 to 12 carbon atoms or a salt thereof.

 [Claim 31] The method for producing a polyhydroxy alkanolate copolymer according to claim 30, wherein for culturing said organism, the peptide to be added to the
20 culture medium is polypeptone; organic acid or salt thereof to be added to the culture medium is one or more compound selected from a group of pyruvic acid, oxaloacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic
25 acid, lactic acid and salts thereof; amino acid or salt thereof to be added to the culture medium is one or more compound selected from a group of glutamic acid,

aspartic acid and salts thereof; and sugar to be added to the culture medium is one or more compound selected from a group of glyceraldehyde, erythrose, arabinose, xylose, glucose, galactose, mannose, fructose, glycerol, 5 erythritol, xylitol, gluconic acid, glucuronic acid, galacturonic acid, maltose, sucrose and lactose.

[Claim 32] The method for producing a polyhydroxy alkanoate copolymer according to any one of claims 27 to 31, characterized in including a step of culturing 10 said microorganism in a culture medium including at least a dicarboxylic acid monoester compound represented by the chemical formula (37) and at least a compound represented by the chemical formula (25) or at least an ω -cyclohexylalkanoic acid represented by the 15 chemical formula (26), and recovering a polyhydroxy alkanoate copolymer including simultaneously at least a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit represented by the chemical formula (32) and a 3-hydroxy- ω -alkanoic acid unit represented by the 20 chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by the chemical formula (3) in the molecule, produced by said microorganism, from cells of the microorganism.

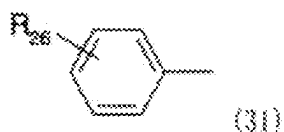
[Claim 33] The method for producing a polyhydroxy 25 alkanoate copolymer according to any one of claims 27 to 32, wherein said microorganism is a microorganism belonging to *Pseudomonas* genus.

[Claim 34] The method for producing a polyhydroxy
alkanoate copolymer according to claim 33, wherein said
microorganism is at least one of *Pseudomonas cichorii*
YN2 strain (FERM BP-7375), *Pseudomonas cichorii* H45
5 strain (FERM BP-7374), *Pseudomonas jessenii* P161 (FERM
BP-7376) and *Pseudomonas putida* P91 (FERM BP-7373).

[Claim 35] The method for producing a polyhydroxy
alkanoate copolymer according to any one of claims 25
to 34, wherein R_{25} in the chemical formula (27) and R_{23}
10 in the chemical formula (25), each representing a
residue having a phenyl structure or a thienyl
structure, represents at least one of chemical formulas
(31), (9), (10), (11), (12), (13), (14), (15), (16),
(17) and (18):

15 the chemical formula (31):

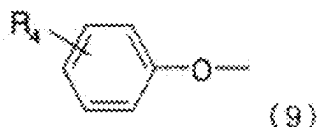
[Chemical Formula 104]



represents a group of substituted or non-substituted
phenyl groups in which R_{26} represents a substituent on
20 an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a CF_3 group, a C_2F_5 group
or a C_3F_7 group; and in case plural units are present,
 R_{26} may be the same or different for each unit;

25 the chemical formula (9):

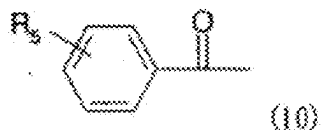
[Chemical Formula 105]



represents a group of non-substituted or substituted
phenoxy groups in which R_4 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or
a C_3F_7 group; and in case plural units are present, R_4
may be the same or different for each unit;

the chemical formula (10):

[Chemical Formula 106]



represents a group of non-substituted or substituted
benzoyl groups in which R_5 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;
and in case plural units are present, R_5 may be the
same or different for each unit;

the chemical formula (11):

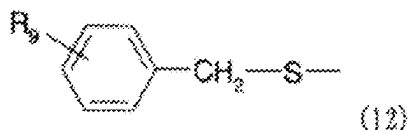
[Chemical Formula 107]



represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

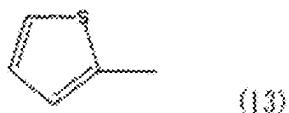
[Chemical Formula 108]



represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{11} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

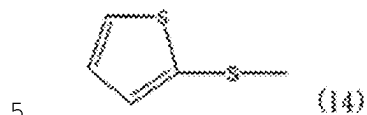
[Chemical Formula 109]



represents a 2-thienyl group;

the chemical formula (14):

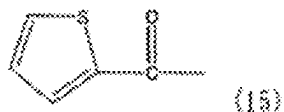
[Chemical Formula 110]



represents a 2-thienylsulfanyl group;

the chemical formula (15):

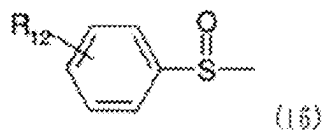
[Chemical Formula 111]



represents a 2-thienylcarbonyl group;

the chemical formula (16):

[Chemical Formula 112]

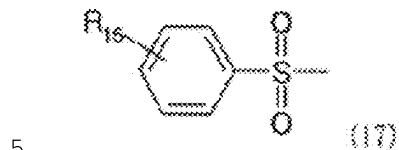


represents a group of substituted or non-substituted
 15 phenylsulfinyl groups in which R_{12} represents a
 substituent on an aromatic ring and represents an H
 atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$
 group, a SO_2R_{14} group (R_{13} representing either one of H,
 Na, K, CH_3 and C_2H_5 ; and R_{14} representing either one of
 20 OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3
 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a

(CH₃)₃-C group; and in case plural units are present,
R₁₂ may be the same or different for each unit;

the chemical formula (17):

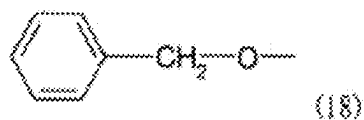
[Chemical Formula 113]



represents a group of substituted or non-substituted
phenylsulfonyl groups in which R₁₅ represents a
substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆
10 group, a SO₂R₁₇ group (R₁₆ representing either one of H,
Na, K, CH₃ and C₂H₅; and R₁₇ representing either one of
OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃
group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a
(CH₃)₃-C group; and in case plural units are present,
15 R₁₅ may be the same or different for each unit; and

the chemical formula (18):

[Chemical Formula 114]



represents a (phenylmethyl)oxy group.

20 [Detailed Description of the Invention]

[0001]

[Field of the invention]

The present invention relates to a polyhydroxy

alkanoate (hereinafter also abbreviated as PHA)
copolymer including a novel unit having a double bond
and a producing method therefor utilizing
microorganisms, also polyhydroxy alkanoate copolymer
5 including a novel unit having a carboxyl group or a
salt thereof, derived from the aforementioned copolymer,
and a producing method therefor.

[0002]

[Background Art]

10 It has already been reported that various
microorganisms produce poly-3-hydroxybutyric acid (PHB)
or other poly-3-hydroxyalkanoate (PHA) and accumulate
such products therein ("Biodegradable Plastic Handbook",
edited by Biodegradable Plastics Society, NTS Inc. pp.
15 178-197 (1995) (Non-patent Document 1)). Such PHA
produced by the microorganisms can be utilized for
producing various products. Also the PHA produced by
microorganisms, being biodegradable, has the advantage
that it can be completely decomposed by the
20 microorganisms. Therefore the PHA produced by
microorganisms, when discarded, unlike the various
conventional synthesized polymers, would not cause
pollution resulting from remaining in the natural
environment. Also the PHA produced by microorganisms
25 shows satisfactory affinity to the living tissues and
is expected in the applications as the soft material
for medical use.

[0003]

It is known that such microorganism-produced PHA can have various compositions and structures depending on the type, medium composition, culturing conditions
5 or the like of microorganisms used for the production. So far studies related to the control of these compositions and structures were mainly conducted from the viewpoint of improving physical properties of PHA.

[0004]

10 [1] First of all, as biosynthesis of PHA, in which monomer units with relatively simple structures are polymerized, including 3-hydroxybutyric acid (hereinafter abbreviated as "3HB"), the following can be pointed out.

15 [0005]

(a) Biosynthesis containing 3HB and 3-hydroxyvaleric acid (hereinafter referred to as "3HV")

Japanese Patent Publication Nos. H6-15604, H7-14352, H8-19227, etc.: Japanese Patent Application
20 Laid-Open No. H5-7492 (Patent Documents 1 to 4)

(b) Biosynthesis containing 3HB and 3-hydroxyhexanoic acid (hereinafter referred to as "3HHx")

Japanese Patent Application Laid-Open Nos. H5-93049 and H7-265065 (Patent Documents 5 and 6)
25

(c) Biosynthesis containing 3HB and 4-hydroxybutyric acid (hereinafter referred to as "4HB")

Japanese Patent Application Laid-Open No. H9-
191893 (Patent Document 7)

(d) Biosynthesis containing 3-hydroxyalkanoate
with 6 to 12 carbon atoms

5 Japanese Patent No. 2642937 (Patent Document 8)

(e) Biosynthesis using a single fatty acid as a
carbon source; the product is almost identical with the
one by (d).

Appl. Environ. Microbiol., 58 (2), 746 (1992)
10 (Non-patent Document 2)

Every one of these is PHA comprised of a monomer
unit having an alkyl group in a side chain synthesized
by β -oxidation of a hydrocarbon or the like or fatty
acid synthesis from a sugar with the help of
15 microorganisms, namely "unusual PHA."

[0006]

[2] However, for wider application of
microorganism-produced PHA, for example for application
as functional polymer, PHA having a substituent other
20 than alkyl group in the side chain, namely "unusual
PHA," is anticipated to be extremely useful. Examples
of hopeful substituents for this purpose include a
group containing an aromatic ring (phenyl group,
phenoxy group etc.), an unsaturated hydrocarbon group,
25 an ester group, an allyl group, a cyano group, a
halogenated hydrocarbon group and an epoxide present on
the side chain. Among these, PHA having an aromatic

ring is actively investigated as follows:

[0007]

(a) PHA containing a phenyl group or a partially substituted group thereof:

5 Makromol. Chem. 191, 1957-1965 (1990) (Non-patent Document 3) and Macromolecules, 24, 5256-5260 (1991) (Non-patent Document 4) report that *Pseudomonas oleovorans* produces PHA containing 3-hydroxy-5-phenylvaleric acid as a unit, from 5-phenylvaleric acid
10 as a substrate.

[0008]

Macromolecules, 29, 1762-1766 (1996) (Non-patent Document 5) reports that *Pseudomonas oleovorans* produces PHA containing 3-hydroxy-5-(p-tolyl)valeric
15 acid as a unit, from 5-(p-tolyl)valeric acid as a substrate.

[0009]

Macromolecules, 32, 2889-2895 (1999) (Non-patent Document 6) reports that *Pseudomonas oleovorans*
20 produces PHA containing 3-hydroxy-5-(2,4-dinitrophenyl)valeric acid and 3-hydroxy-5-(p-nitrophenyl)valeric acid as units, from 5-(2,4-dinitrophenyl)valeric acid as a substrate.

[0010]

25 (b) PHA containing phenoxy group or a partially substituted group thereof:

Macromol. Chem. Phys., 195, 1665-1672 (1994) (Non-

patent Document 7) reports that *Pseudomonas oleovorans* produces a PHA copolymer containing 3-hydroxy-5-hydroxyvaleric acid and 3-hydroxy-9-phenoxyundecanoic acid as the units, from 11-phenoxyundecanoic acid as a
5 substrate.

[0011]

Also Japanese Patent No. 2989175 (Patent Document 8) discloses inventions relating to a homopolymer constituted of a 3-hydroxy-5-(monofluorophenoxy)
10 pentanoate (3H5(MFP)P) unit or a 3-hydroxy-5-(difluorophenoxy) pentanoate (3H5(DFP)P) unit, a copolymer containing either a 3H5(MFP)P unit or a 3H5(DFP)P unit or both, a novel strain of *Pseudomonas putida* capable of producing these polymers, and a
15 method for producing the aforementioned polymers utilizing bacteria of genus *Pseudomonas*. This patent specification teaches, as the effects of such inventions, that PHA polymer having a phenoxy group substituted with 1 or 2 fluorine atoms at the end of
20 the side chain can be biosynthesized from a long-chain fatty acid having a fluorine substituent and that thus produced PHA has a high melting point and is capable of providing stereoregularity and water repellency while maintaining satisfactory working properties.

25 [0012]

In addition to the fluorine-substituted PHA having a fluorine substitution on the aromatic ring in the

unit, there are also investigated PHA having a cyano group or a nitro group on the aromatic ring in the unit.

[0013]

Can. J. Microbiol., 41, 32-43 (1995) (Non-patent
5 Document 8) and Polymer International, 39, 205-213
(1996) (Non-patent Document 9) report production of PHA,
containing 3-hydroxy-6-(p-cyanophenoxy) hexanoic acid
or 3-hydroxy-6-(p-nitrophenoxy) hexanoic acid as the
monomer unit, by *Pseudomonas oleovorans* ATCC 29347
10 strain and *Pseudomonas putida* KT2442 strain, from
octanoic acid and 6-(p-cyanophenoxy) hexanoic acid or
6-(p-nitrophenoxy) hexanoic acid as a substrate.

[0014]

These references relate to PHA having an aromatic
15 ring on the side chain, instead of alkyl groups of the
usual PHA, which are effective in obtaining polymer
with physical properties resulting from such aromatic
ring.

[0015]

20 [3] Also as a new category not limited to changes
in the physical properties, investigations are also
made for producing PHA having an appropriate functional
group on the side chain, thereby obtaining PHA with new
functions utilizing such substituent.

25 [0016]

As a specific method for such purpose,
investigations are also made for producing PHA having,

in a unit thereof, reactive group such as a bromo group
or a vinyl group with a high activity for example in an
addition reaction to introduce an arbitrary function
group in a side chain of the polymer by a chemical
5 conversion utilizing such active group, in order to
obtain PHA of multiple functions.

[0017]

Macromol. Rapid Commun., 20, 91-94 (1999) (Non-
patent Document 10) reports production of PHA having a
10 bromo group in a side chain by *Pseudomonas oleovorans*,
and modifying the side chain with a thiolated product
of acetylated maltose thereby synthesizing PHA
different in solubility and hydrophilicity.

[0018]

15 Polymer, 41, 1703-1709 (2000) (Non-patent Document
11) reports producing PHA, having 3-hydroxyalkenic acid
with an unsaturated bond (vinyl group) at an end of a
side chain as a monomer unit, by *Pseudomonas oleovorans*
with 10-undecenoic acid as a substrate, followed by an
20 oxidation reaction with potassium permanganate to
synthesize 3-hydroxyalkanoic acid having a diol at the
end of the side chain, which PHA is reported to show
such a change in solubility in solvents, as becoming
soluble in polar solvents such as methanol, an acetone-
25 water (80/20, v/v) or dimethylsulfoxide and insoluble
in non-polar solvents such as chloroform,
tetrahydrofuran or acetone.

[0019]

Also *Macromolecules*, 31, 1480-1486 (1996) (Non-patent Document 12) reports production of a polyester, including a unit having vinyl group in a side chain by
5 *Pseudomonas oleovorans* and epoxylating the vinyl group to obtain a polyester having an epoxy group in the side chain.

[0020]

Also *Polymer*, 35, 2090-2097 (1994) (Non-patent
10 Document 13) reports a crosslinking reaction within the polyester molecule utilizing the vinyl group in the side chain of polyester, thereby improving physical properties of polyester.

[0021]

15 *Macromolecular chemistry*, 4, 289-293 (2001) (Non-patent Document 14) reports producing PHA, including 3-hydroxy-10-undecenoic acid as a monomer unit, from 10-undecenoic acid as a substrate, and then executing an oxidation reaction with potassium permanganate to
20 obtain PHA including 3-hydroxy-10-carboxydecanoic acid as a monomer unit, and reports an improvement in a decomposition thereof.

[0022]

Furthermore, in order to modify physical
25 properties of PHA having an active group in a unit and to actually utilize it as a polymer, it has been studied biosynthesis of a PHA copolymer including a

unit having the active group and other units;
Macromolecules, 25, 1852-1857 (1992) (Non-patent
Document 15) reports production of a PHA copolymer
including a 3-hydroxy- ω -bromoalkanoic acid unit and a
5 linear alkanoic acid unit by *Pseudomonas oleovorans* in
the presence of an ω -bromoalkanoic acid such as 11-
bromoundecanoic acid, 8-bromooctanoic acid or 6-
bromohexanoic acid and n-nonanoic acid.

[0023]

10 Such PHA having a highly reactive active group
such as a bromo group or a vinyl group can be subjected
to introduction of various functional groups or
chemical modification, and such a group can be a
crosslinking point for a polymer, so that it is very
15 useful means for realizing multiple functions in PHA.

[0024]

Also technologies related to the present invention
include a technology of oxidizing and cleaving a
carbon-carbon double bond with an oxidant to obtain a
20 carboxylic acid (Patent Document 9 and Non-patent
Documents 16 to 19)

[0025]

[Patent Document 1]

Japanese Patent Publication No. H6-15604

25 [Patent Document 2]

Japanese Patent Publication No. H7-14352

[Patent Document 3]

- Japanese Patent Publication No. H8-19227
[Patent Document 4]
Japanese Patent Application Laid-Open No. H5-7492
[Patent Document 5]
5 Japanese Patent Application Laid-Open No. H5-93049
[Patent Document 6]
Japanese Patent Application Laid-Open No. H7-
265065
[Patent Document 7]
10 Japanese Patent Application Laid-Open No. H9-
191893
[Patent Document 8] Japanese Patent No. 2989175
[Patent Document 9]
Japanese Patent Application Laid-Open No. S59-
15 190945
[0026]
[Non-patent Document 1]
"Biodegradable Plastic Handbook", edited by
Biodegradable Plastics Society, NTS Inc. pp. 178-197
20 (1995)
[Non-patent Document 2]
Appl. Environ. Microbiol., 58 (2), 746 (1992)
[Non-patent Document 3]
Makromol. Chem. 191, 1957-1965 (1990)
25 [Non-patent Document 4]
Macromolecules, 24, 5256-5260 (1991)
[Non-patent Document 5]

- Macromolecules, 29, 1762-1766 (1996)
[Non-patent Document 6]
Macromolecules, 32, 2889-2895 (1999)
[Non-patent Document 7]
5 Macromol. Chem. Phys., 195, 1665-1672 (1994)
[Non-patent Document 8]
Can. J. Microbiol., 41, 32-43 (1995)
[Non-patent Document 9]
Polymer International, 39, 205-213 (1996)
10 [Non-patent Document 10]
Macromol. Rapid Commun., 20, 91-94 (1999)
[Non-patent Document 11]
Polymer, 41, 1703-1709 (2000)
[Non-patent Document 12]
15 Macromolecules, 31, 1480-1486 (1996)
[Non-patent Document 13]
Polymer, 35, 2090-2097 (1994)
[Non-patent Document 14] Macromolecular chemistry, 4,
289-293 (2001)
20 [Non-patent Document 15]
Macromolecules, 25, 1852-1857 (1992)
[Non-patent Document 16]
J. Chem. Soc., Perkin. Trans. 1, 806 (1973)
[Non-patent Document 17]
25 Org. Synth., 4, 698 (1963)
[Non-patent Document 18]
J. Org. Chem., 46, 19 (1981)

[Non-patent Document 19]

J. Am. Chem. Soc., 81, 4273 (1959)

[0027]

[Problem to be Solved by the Invention]

5 However, the copolymers in the foregoing reports
are comprised of a monomer unit having a carboxyl group
at the end of a side chain and a monomer unit having a
linear alkyl group (usual PHA). Because of this, this
polymer has problems, such as a low glass transition
10 temperature. On the other hand, there is no report on
copolymers including unusual PHA having on the side
chain thereof a substituent other than a linear alkyl
group, such as a phenyl structure, a thienyl structure
or a cyclohexyl structure. Thus such polyhydroxy
15 alkanoate and a producing method therefor have been
required.

[0028]

 Also PHA having a vinyl group as an active group
is a PHA copolymer with a monomer unit having a linear
20 alkyl group (usual PHA), its low glass transition
temperature and low melting point are undesirable
properties in the working and the use of the polymer.

[0029]

 Because of the above-described situation, there
25 have been a demand for PHA having an active group and a
production method therefor, such that PHA can be
produced by a microorganism at a high yield, the unit

ratio of the active group can be controlled, and its physical properties can be freely regulated not to limit its application as a polymer.

[0030]

5 [Means for Solving the Problem]

As a result of intensive investigations, the present inventors have found a method of synthesizing a PHA formed by copolymerization of a unit having a vinyl group or a carboxyl group of a high reactivity, and a
10 unit having either one of a phenyl structure, a thienyl structure and a cyclohexyl structure which can contribute to an improvement of physical properties of the polymer, and have thus made the present invention.

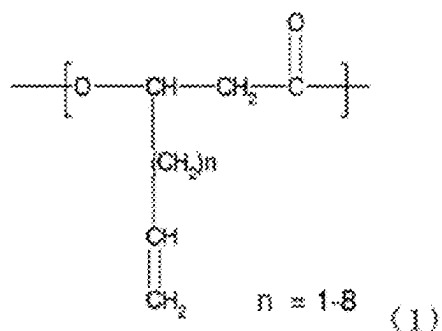
The present invention is outlined in the following.

15 [0031]

[1] A polyhydroxy alkanooate copolymer characterized in including at least a 3-hydroxy- ω -alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-
20 hydroxy- ω -alkanoic acid unit represented by a chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[0032]

25 [Chemical Formula 115]

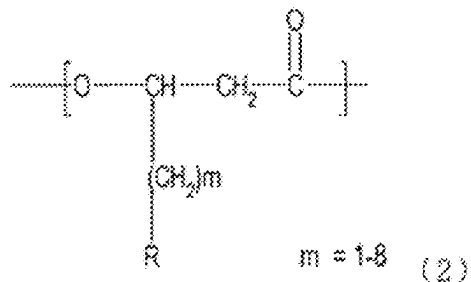


[0033]

in which n represents an integer selected within a
range indicated in the chemical formula; and in case
5 plural units are present, n may be the same or
different for each unit;

[0034]

[Chemical Formula 116]

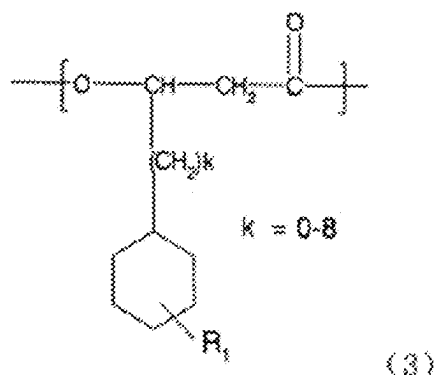


10 [0035]

in which m represents an integer selected within a
range indicated in the chemical formula; R represents a
residue having any of a phenyl structure or a thienyl
structure; and in case plural units are present, m and
15 R may be the same or different for each unit;

[0036]

[Chemical Formula 117]



[0037]

in which R_1 being a substituent on a cyclohexyl group represents a hydrogen atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit.

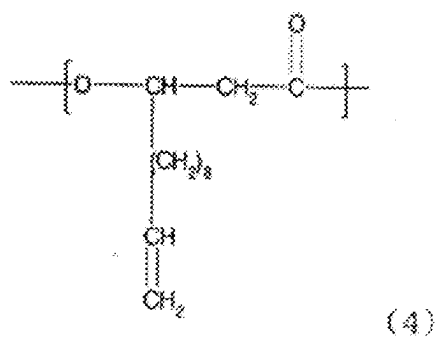
[2] The polyhydroxy alkanate copolymer according to [1], wherein the 3-hydroxy- ω -alkenoic acid unit represented by the chemical formula (1) is any one of

[0038]

a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

[0039]

[Chemical Formula 118]

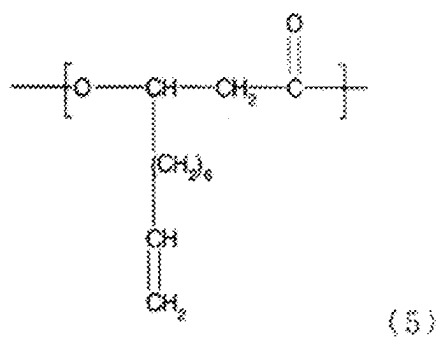


[0040]

a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

5 [0041]

[Chemical Formula 119]



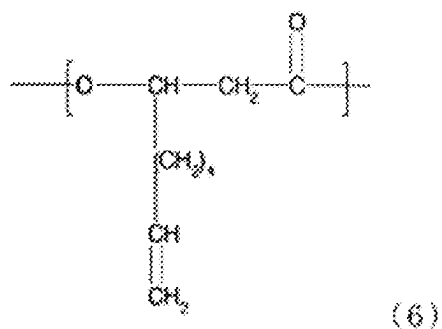
[0042]

a 3-hydroxy-8-nonenoic acid unit represented by a chemical formula (6): and

10

[0043]

[Chemical Formula 120]

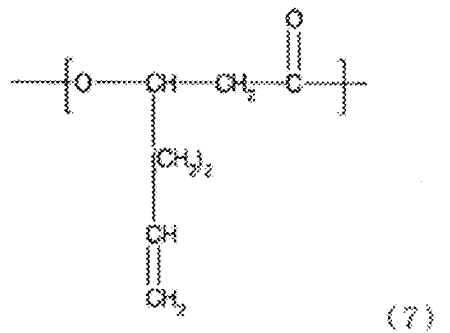


[0044]

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7):

5 [0045]

[Chemical Formula 121]



[0046]

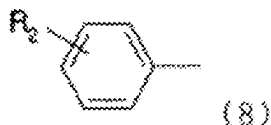
[3] The polyhydroxy alkanoate copolymer according to [1] or [2], wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from the group consisting of chemical formulas (8), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

15 [0047]

the chemical formula (8):

[0048]

[Chemical Formula 122]



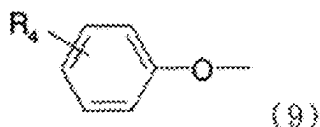
[0049]

represents a group of non-substituted or substituted
5 phenyl groups in which R_2 , a substituent on an aromatic
ring and represents an H atom, represents a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a COOR_3 group (R_3
represents an H atom, a Na atom or a K atom), a CF_3
10 group, a C_2F_5 group, or a C_3F_7 group; and in case plural
units are present, R_2 may be the same or different for
each unit;

the chemical formula (9):

[0050]

15 [Chemical Formula 123]



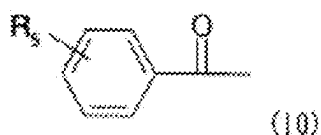
[0051]

represents a group of non-substituted or substituted
phenoxy groups in which R_4 represents a substituent on
20 an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or
a C_3F_7 group; and in case plural units are present, R_4
may be the same or different for each unit;

the chemical formula (10):

[0052]

[Chemical Formula 124]



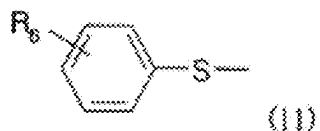
5 [0053]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, 10 a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11)

[0054]

15 [Chemical Formula 125]



[0055]

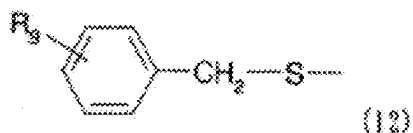
represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a 20 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 represents either one of OH, ONa,

OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and in case plural units are present, R_6 may be the same or different for each unit;

5 the chemical formula (12):

[0056]

[Chemical Formula 126]



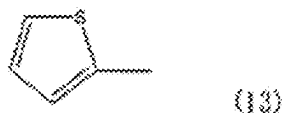
[0057]

10 represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a COOR_{10} group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and in case plural units are present, R_9 may be the same or different for each unit;

20 the chemical formula (13):

[0058]

[Chemical Formula 127]



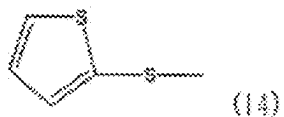
[0059]

represents a 2-thienyl group;

the chemical formula (14)

[0060]

5 [Chemical Formula 128]



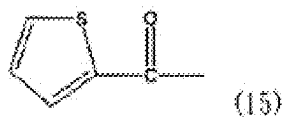
[0061]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

10 [0062]

[Chemical Formula 129]



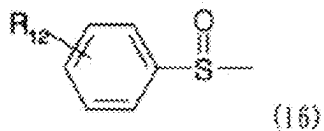
[0063]

represents a 2-thienylcarbonyl group;

15 the chemical formula (16):

[0064]

[Chemical Formula 130]



[0065]

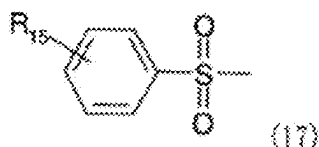
20 represents a group of substituted or non-substituted
phenylsulfinyl groups in which R_{12} represents a
substituent on an aromatic ring and represents an H

atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₃ group, a SO₂R₁₄ group (R₁₃ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₄ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
5 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₂ may be the same or different for each unit;

the chemical formula (17):

[0066]

10 [Chemical Formula 131]



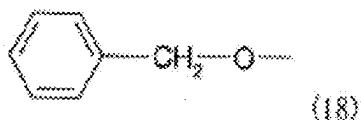
[0067]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R₁₅ represents a
15 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆ group, a SO₂R₁₇ group (R₁₆ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₇ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
20 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₅ may be the same or different for each unit; and

the chemical formula (18):

[0068]

25 [Chemical Formula 132]



[0069]

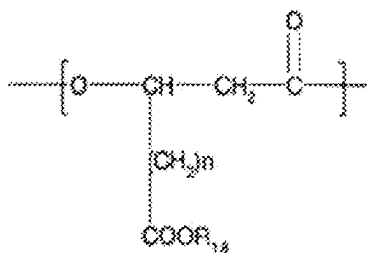
represents a (phenylmethyl)oxy group.

[0070]

- 5 [4] A polyhydroxy alkanoate copolymer characterized in including at least a 3-hydroxy- ω -carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a
- 10 chemical formula (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule,

[0071]

[Chemical Formula 133]



$n = 1-8$ (19)

15

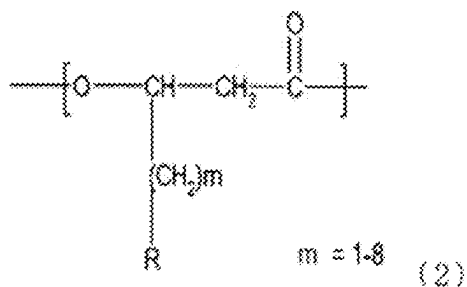
[0072]

- in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom or a K atom: and in case plural
- 20 units are present, n and R_{18} may be the same or

different for each unit;

[0073]

[Chemical Formula 134]



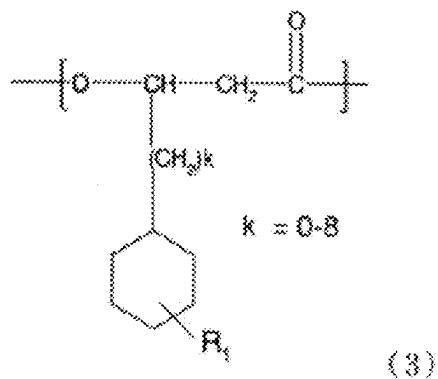
5 [0074]

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and

10 R may be the same or different for each unit; and

[0075]

[Chemical Formula 135]



[0076]

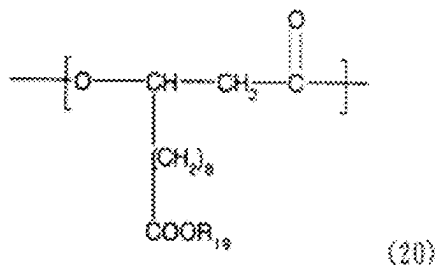
15 in which R₁ represents a substituent on a cyclohexyl
group and represents an H atom, a CN group, a NO₂ group,

a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group,
a CF₃ group, a C₂F₅ group, or a C₃F₇ group; k represents
an integer selected within a range indicated in the
chemical formula; and in case plural units are present,
5 R₁ and k may be the same or different for each unit.

[5] The polyhydroxy alkanoate copolymer according
to [4], wherein the 3-hydroxy-ω-carboxyalkanoic acid
unit represented by the chemical formula (19) is any
one of a 3-hydroxy-11-carbonylundecanoic acid unit
10 represented by a chemical formula (20):

[0077]

[Chemical Formula 136]



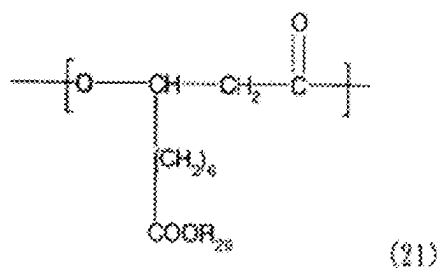
(20)

[0078]

15 (R₁₉ represents an H atom, a Na atom or a K atom; and
in case plural units are present, R₁₉ may be the same
or different for each unit),
a 3-hydroxy-9-carboxynonanoic acid unit represented by
a chemical formula (21):

20 [0079]

[Chemical Formula 137]

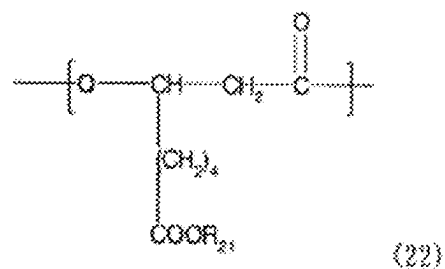


[0080]

(R₂₀ represents an H atom, a Na atom or a K atom and in case plural units are present; and R₂₀ may be the same
5 or different for each unit),
a 3-hydroxy-7-carboxyheptanoic acid unit represented by
a chemical formula (22):

[0081]

[Chemical Formula 138]



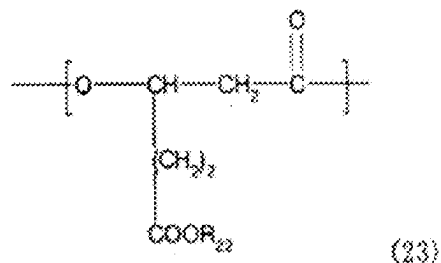
10

[0082]

(R₂₁ represents an H atom, a Na atom or a K atom; and
in case plural units are present, R₂₁ may be the same
or different for each unit), and
15 a 3-hydroxy-5-carboxyvaleric acid unit represented by a
chemical formula (23):

[0083]

[Chemical Formula 139]



[0084]

(R₂₂ represents an H atom, a Na atom or a K atom; and
in case plural units are present, R₂₂ may be the same
5 or different for each unit).

[0085]

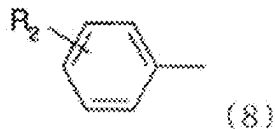
[6] The polyhydroxy alkanoate copolymer according
to [4] or [5], wherein R in the chemical formula (2),
represents a residue having a phenyl structure or a
10 thienyl structure selected from chemical formulas (8),
(9), (10), (11), (12), (13), (14), (15), (16), (17),
and (18):

[0086]

the chemical formula (8):

15 [0087]

[Chemical Formula 140]



[0088]

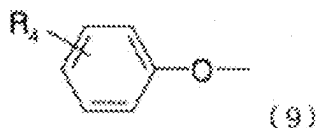
represents a group of non-substituted or substituted
20 phenyl groups in which R₂ represents a substituent on
an aromatic ring and represents an H atom, a halogen

atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group,
a C₃H₇ group, a CH=CH₂ group, a COOR₃ group (R₃
representing an H atom, a Na atom or a K atom), a CF₃
group, a C₂F₅ group, or a C₃F₇ group; and in case plural
5 units are present, R₂ may be the same or different for
each unit;

the chemical formula (9):

[0089]

[Chemical Formula 141]



10

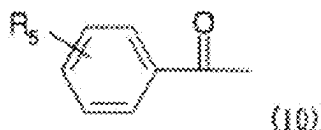
[0090]

represents a group of non-substituted or substituted
phenoxy groups in which R₄ represents a substituent on
an aromatic ring and represents an H atom, a halogen
15 atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group,
a C₃H₇ group, a SCH₃ group, a CF₃ group, a C₂F₅ group, or
a C₃F₇ group; and in case plural units are present, R₄
may be the same or different for each unit;

the chemical formula (10):

20 [0091]

[Chemical Formula 142]



[0092]

represents a group of non-substituted or substituted benzoyl groups in which R_5 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
5 a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;
and in case plural units are present, R_5 may be the same or different for each unit;

the chemical formula (11):

[0093]

10 [Chemical Formula 143]



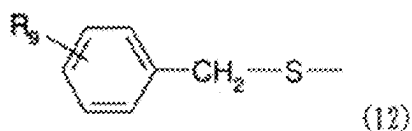
[0094]

represents a group of substituted or non-substituted phenylsulfanyl groups in which R_6 represents a
15 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a COOR_7 group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5
20 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0095]

25 [Chemical Formula 144]



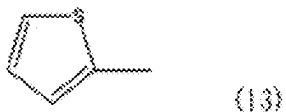
[0096]

represents a group of substituted or non-substituted
(phenylmethyl)sulfanyl groups in which R₉ represents a
5 substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀
group, a SO₂R₁₁ group (R₁₀ represents either one of H,
Na, K, CH₃ and C₂H₅; and R₁₁ represents either one of OH,
ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a
10 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C
group; and in case plural units are present, R₉ may be
the same or different for each unit;

the chemical formula (13):

[0097]

15 [Chemical Formula 145]



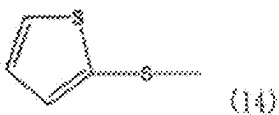
[0098]

represents a 2-thienyl group;

the chemical formula (14):

20 [0099]

[Chemical Formula 146]



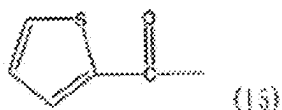
[0100]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0101]

5 [Chemical Formula 147]



[0102]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

10 [0103]

[Chemical Formula 148]



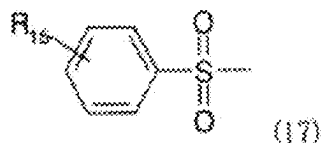
[0104]

represents a group of substituted or non-substituted
15 phenylsulfinyl groups in which R_{12} represents a
substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$
group, a SO_2R_{14} group (R_{13} represents either one of H,
Na, K, CH_3 and C_2H_5 ; and R_{14} represents either one of OH,
20 ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a
 C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$
group; and in case plural units are present, R_{12} may be
the same or different for each unit;

the chemical formula (17):

[0105]

[Chemical Formula 149]



[0106]

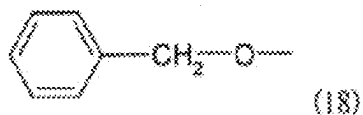
5 represents a group of substituted or non-substituted phenylsulfonyl groups in which R₁₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆ group, a SO₂R₁₇ group (R₁₆ represents either one of H,

10 Na, K, CH₃ and C₂H₅; and R₁₇ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₅ may be the same or different for each unit; and

15 the chemical formula (18):

[0107]

[Chemical Formula 150]



[0108]

20 represents a (phenylmethyl)oxy group.

[0109]

[7] The polyhydroxy alkanoate copolymer according to any one of [1] to [6], wherein a number-averaged

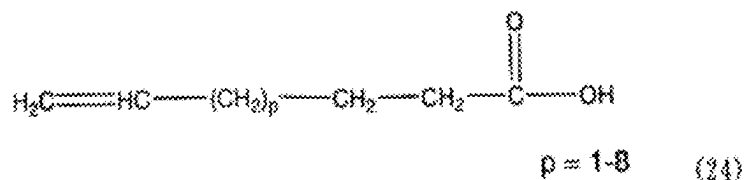
molecular weight is within a range from 1000 to 1000000.

[0110]

[8] A method for producing a polyhydroxy
alkanoate copolymer characterized in including a
5 biosynthesis by a microorganism having an ability of
producing a polyhydroxy alkanoate copolymer including
at least a 3-hydroxy- ω -alkenoic acid unit represented
by a chemical formula (1) in a molecule, and
simultaneously at least a 3-hydroxy- ω -alkanoic acid
10 unit represented by a chemical formula (2) or a 3-
hydroxy- ω -cyclohexylalkanoic acid unit represented by a
chemical formula (3) in the molecule, from at least an
 ω -alkenoic acid represented by a chemical formula (24)
and at least a compound represented by a chemical
15 formula (25) or at least an ω -cyclohexylalkanoic acid
represented by a chemical formula (26) as starting
materials:

[0111]

[Chemical Formula 151]



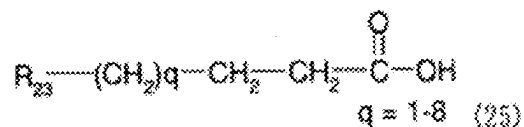
20

[0112]

in which p represents an integer selected within a
range indicated in the chemical formula;

[0113]

[Chemical Formula 152]

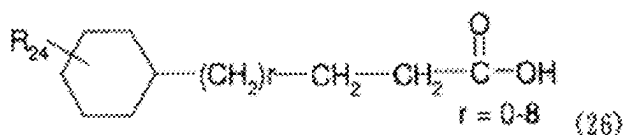


[0114]

in which q represents an integer selected within a
 5 range indicated in the chemical formula; and R_{23}
 includes a residue having a phenyl structure or a
 thienyl structure;

[0115]

[Chemical Formula 153]



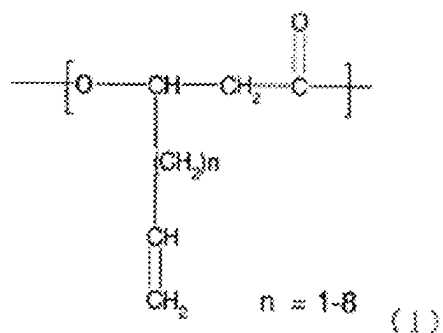
10

[0116]

in which R_{24} represents a substituent on a cyclohexyl
 group and represents an H atom, a CN group, a NO_2 group,
 a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group,
 15 a CF_3 group, a C_2F_5 group, or a C_3F_7 group; and r
 represents an integer selected within a range indicated
 in the chemical formula;

[0117]

[Chemical Formula 154]

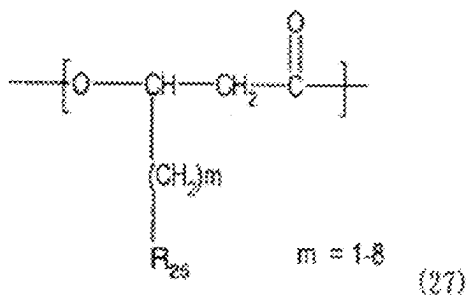


[0118]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0119]

[Chemical Formula 155]

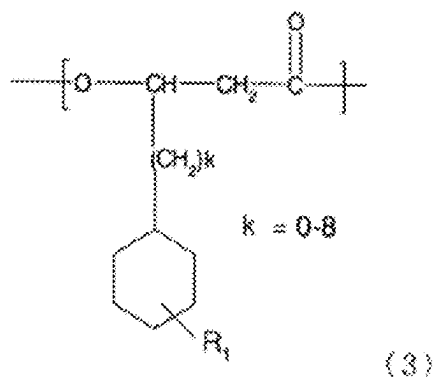


10 [0120]

in which m represents an integer selected within a range indicated in the chemical formula; R₂₅ represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R₂₅ may be the same or different for each unit; and

[0121]

[Chemical Formula 156]



[0122]

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

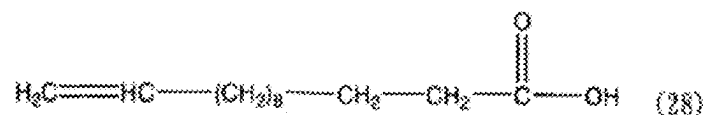
[9] The method for producing a polyhydroxy alkananoate copolymer according to [8], wherein the ω -alkenoic acid represented by the chemical formula (24) is

[0123]

a 12-tridecenoic acid represented by a chemical formula (28): or

[0124]

[Chemical Formula 157]



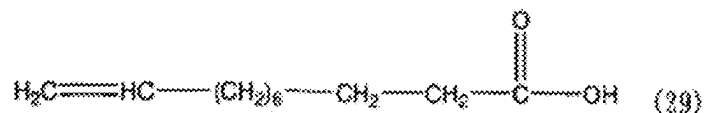
[0125]

a 10-undecenoic acid represented by a chemical formula

(29): or

[0126]

5 [Chemical Formula 158]

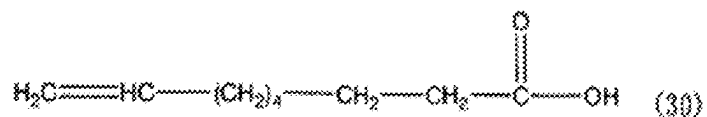


[0127]

a 8-nonenoic acid unit represented by a chemical formula (30):

10 [0128]

[Chemical Formula 159]



[0129]

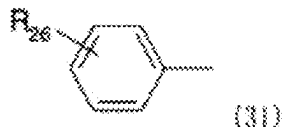
[10] The method for producing a polyhydroxy
15 alkanooate copolymer according to [8] or [9], wherein
R₂₃ in the chemical formula (25) and R₂₅ in the chemical
formula (27), each represents a residue having a phenyl
structure or a thienyl structure, are selected from
chemical formulas (31), (9), (10), (11), (12), (13),
20 (14), (15), (16), (17) and (18):

[0130]

the chemical formula (31):

[0131]

[Chemical formula 160]



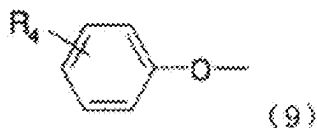
[0132]

represents a group of substituted or non-substituted
5 phenyl groups in which R_{26} represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a CF_3 group, a C_2F_5 group
or a C_3F_7 group; and in case plural units are present,
10 R_{26} may be the same or different for each unit;

the chemical formula (9):

[0133]

[Chemical Formula 161]



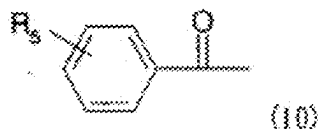
15 [0134]

represents a group of non-substituted or substituted
phenoxy groups in which R_4 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
20 a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or
a C_3F_7 group; and in case plural units are present, R_4
may be the same or different for each unit;

the chemical formula (10):

[0135]

[Chemical Formula 162]



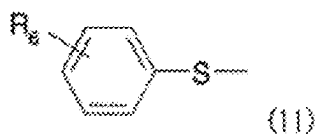
[0136]

represents a group of non-substituted or substituted
 5 benzoyl groups in which R_5 represents a substituent on
 an aromatic ring and represents an H atom, a halogen
 atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
 a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;
 and in case plural units are present, R_5 may be the
 10 same or different for each unit;

the chemical formula (11):

[0137]

[Chemical Formula 163]



15 [0138]

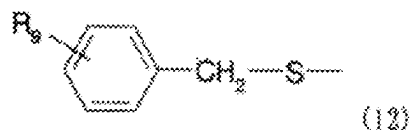
represents a group of substituted or non-substituted
 phenylsulfanyl groups in which R_6 represents a
 substituent on an aromatic ring and represents an H
 atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$
 20 group, a SO_2R_8 group (R_7 representing either one of H,
 Na, K, CH_3 and C_2H_5 ; and R_8 representing either one of
 OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3
 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a

(CH₃)₃-C group; and in case plural units are present, R₆ may be the same or different for each unit;

the chemical formula (12):

[0139]

5 [Chemical Formula 164]



[0140]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R₉ represents a
10 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀ group, a SO₂R₁₁ group (R₁₀ representing either one of H, Na, K, CH₃ and C₂H₅; and R₁₁ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃
15 group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₉ may be the same or different for each unit;

the chemical formula (13):

[0141]

20 [Chemical Formula 165]



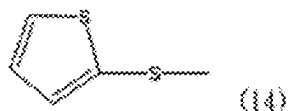
[0142]

represents a 2-thienyl group;

the chemical formula (14):

[0143]

[Chemical Formula 166]



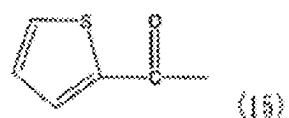
5 [0144]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0145]

[Chemical Formula 167]



10

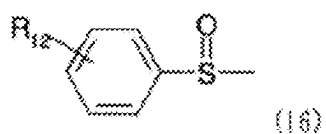
[0146]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0147]

15 [Chemical Formula 168]



[0148]

represents a group of substituted or non-substituted
phenylsulfinyl groups in which R₁₂ represents a
20 substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₃
group, a SO₂R₁₄ group (R₁₃ representing either one of H,

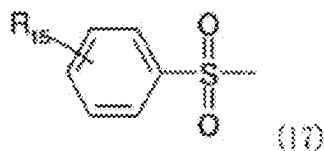
Na, K, CH₃ and C₂H₅; and R₁₄ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present,

5 R₁₂ may be the same or different for each unit;

the chemical formula (17):

[0149]

[Chemical Formula 169]



10 [0150]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R₁₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆

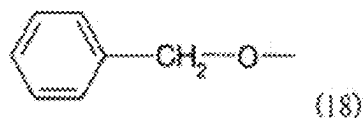
15 group, a SO₂R₁₇ group (R₁₆ representing either one of H, Na, K, CH₃ and C₂H₅; and R₁₇ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present,

20 R₁₅ may be the same or different for each unit; and

the chemical formula (18):

[0151]

[Chemical Formula 170]



[0152]

represents a (phenylmethyl)oxy group.

[0153]

5 [11] The method for producing a polyhydroxy
alkanoate copolymer according to any one of [8] to [10],
wherein the microorganism is cultured in a culture
medium including at least a ω -alkenoic acid represented
by the chemical formula (24) and at least a compound
10 represented by the chemical formula (25) or at least a
 ω -cyclohexylalkanoic acid represented by the chemical
formula (26).

[0154]

 [12] The method for producing a polyhydroxy
15 alkanoate copolymer according to [11], wherein the
microorganism is cultured in a culture medium including,
in addition to at least an ω -alkenoic acid represented
by the chemical formula (24) and at least a compound
represented by the chemical formula (25) or at least a
20 ω -cyclohexylalkanoic acid represented by the chemical
formula (26), at least one of a peptide, an yeast
extract, an organic acid or a salt thereof, an amino
acid or a salt thereof, a sugar, a linear alkanoic acid
with 4 to 12 carbon atoms or a salt thereof.

25 [0155]

[13] The method for producing a polyhydroxy

alkanoate copolymer according to [12] wherein for
culturing the organism, the peptide to be added to the
culture medium is polypeptone; organic acid or salt
thereof to be added to the culture medium is one or
5 more compound selected from a group of piruvic acid,
oxaloacetic acid, citric acid, isocitric acid,
ketoglutaric acid, succinic acid, fumaric acid, malic
acid, lactic acid and salts thereof; amino acid or salt
thereof to be added to the culture medium is one or
10 more compound selected from a group of glutamic acid,
aspartic acid and salts thereof; and sugar to be added
to the culture medium is one or more compound selected
from a group of glyceraldehyde, erythrose, arabinose,
xylose, glucose, galactose, mannose, fructose, glycerol,
15 erythritol, xylitol, gluconic acid, glucuronic acid,
galacturonic acid, maltose, sucrose and lactose.
[0156]

[14] The method for producing a polyhydroxy
alkanoate copolymer according to any one of [8] to [13],
20 characterized in including a step of culturing the
microorganism in a culture medium including at least an
 ω -alkenoic acid represented by the chemical formula
(24) and at least a compound represented by the
chemical formula (25) or at least an ω -
25 cyclohexylalkanoic acid represented by the chemical
formula (26), and recovering a polyhydroxy alkanoate
copolymer including simultaneously at least a 3-

hydroxy- ω -alkenoic acid unit represented by the
chemical formula (1) and a 3-hydroxy- ω -alkanoic acid
unit represented by the chemical formula (2) or a 3-
hydroxy- ω -cyclohexylalkanoic acid unit represented by
5 the chemical formula (3) in the molecule, produced by
the microorganism, from cells of the microorganism.
[0157]

[15] The method for producing a polyhydroxy
alkanoate copolymer according to any one of [8] to [14],
10 wherein the microorganism is a microorganism belonging
to *Pseudomonas* genus.
[0158]

[16] The method for producing a polyhydroxy
alkanoate copolymer according to [15], wherein the
15 microorganism is at least one of *Pseudomonas cichorii*
YN2 strain (FERM BP-7375), *Pseudomonas cichorii* H45
strain (FERM BP-7374), *Pseudomonas jessenii* P161 (FERM
BP-7376) and *Pseudomonas putida* P91 (FERM BP-7373).
[0159]

20 [17] A method for producing a polyhydroxy
alkanoate copolymer including at least a 3-hydroxy- ω -
carboxyalkanoic acid unit represented by a chemical
formula (19) in a molecule, and simultaneously at least
a 3-hydroxy- ω -alkanoic acid unit represented by a
25 chemical formula (2) or a 3-hydroxy- ω -
cyclohexylalkanoic acid unit represented by a chemical
formula (3) in the molecule comprising the steps of:

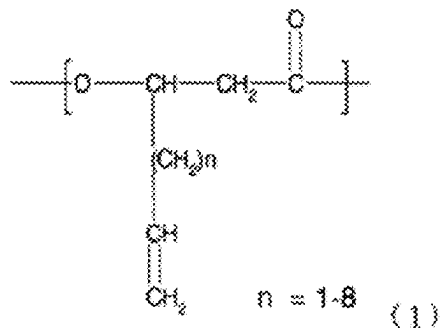
preparing a polyhydroxy alkanoate copolymer including
 at least a 3-hydroxy- ω -alkenoic acid unit represented
 by a chemical formula (1) in a molecule, and
 simultaneously at least a 3-hydroxy- ω -alkanoic acid
 5 unit represented by a chemical formula (2) or a 3-
 hydroxy- ω -cyclohexylalkanoic acid unit represented by a
 chemical formula (3) in the molecule as a starting
 material, and

oxidizing and cleaving a double bond portion in
 10 the polyhydroxy alkanoate represented in the chemical
 formula (1) thereby

generating a polyhydroxy alkanoate copolymer
 including at least a 3-hydroxy- ω -carboxyalkanoic acid
 unit represented by a chemical formula (19) in a
 15 molecule, and simultaneously at least a 3-hydroxy- ω -
 alkenoic acid unit represented by a chemical formula
 (2) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit
 represented by a chemical formula (3) in the molecule:

[0160]

20 [Chemical Formula 171]

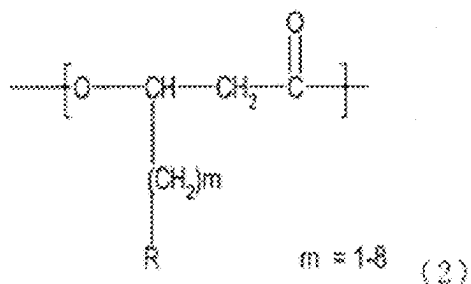


[0161]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

5 [0162]

[Chemical Formula 172]

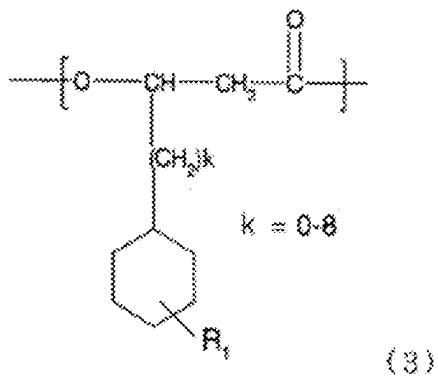


[0163]

in which m represents an integer selected within a range indicated in the chemical formula; R includes a residue having any of a phenyl structure and a thienyl structure; and in case plural units are present, m and R may be the same or different for each unit;

[0164]

15 [Chemical Formula 173]

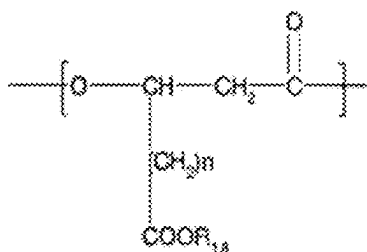


[0165]

in which R_1 represents a substituent on a cyclohexyl group selected from an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, and a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 and k may be the same or different for each unit; and

10 [0166]

[Chemical Formula 174]



$n = 1-8$ (19)

[0167]

in which n represents an integer selected within a range indicated in the chemical formula; R_{18} represents an H atom, a Na atom, or a K atom; and in case plural units are present, n and R_{18} may be the same or different for each unit.

[18] The method for producing a polyhydroxy alkananoate copolymer according to [17], wherein R in the chemical formula (2) represents a residue having a phenyl structure or a thienyl structure selected from

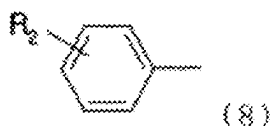
chemical formulas (8), (9), (10), (11), (12), (13),
(14), (15), (16), (17) and (18):

[0168]

the chemical formula (8):

5 [0169]

[Chemical Formula 175]



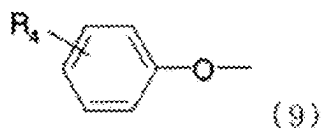
[0170]

represents a group of non-substituted or substituted
10 phenyl groups in which R_2 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a $\text{CH}=\text{CH}_2$ group, a COOR_3 group (R_3
representing an H atom, a Na atom or a K atom), a CF_3
15 group, a C_2F_5 group, or a C_3F_7 group; and in case plural
units are present, R_2 may be the same or different for
each unit;

the chemical formula (9):

[0171]

20 [Chemical Formula 176]



[0172]

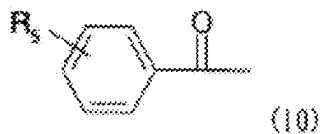
represents a group of non-substituted or substituted
phenoxy groups in which R_4 represents a substituent on

an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a SCH₃ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and in case plural units are present, R₄ may be the same or different for each unit;

the chemical formula (10):

[0173]

[Chemical Formula 177]



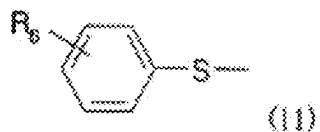
10 [0174]

represents a group of non-substituted or substituted benzoyl groups in which R₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and in case plural units are present, R₅ may be the same or different for each unit;

the chemical formula (11):

[0175]

20 [Chemical Formula 178]



[0176]

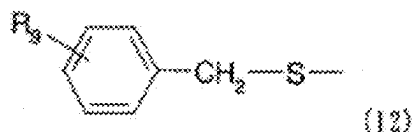
represents a group of substituted or non-substituted

phenylsulfanyl groups in which R_6 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$ group, a SO_2R_8 group (R_7 represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_8 represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_6 may be the same or different for each unit;

the chemical formula (12):

[0177]

[Chemical Formula 179]



[0178]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R_9 represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{10}$ group, a SO_2R_{11} group (R_{10} represents either one of H, Na, K, CH_3 and C_2H_5 ; and R_{11} represents either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present, R_9 may be the same or different for each unit;

the chemical formula (13):

[0179]

[Chemical Formula 180]

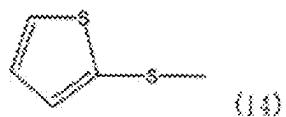


[0180]

5 represents a 2-thienyl group;
the chemical formula (14):

[0181]

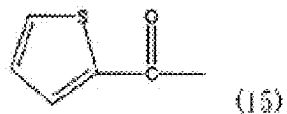
[Chemical Formula 181]



10 [0182]
represents a 2-thienylsulfanyl group;
the chemical formula (15):

[0183]

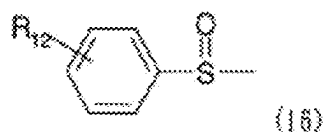
[Chemical Formula 182]



15 [0184]
represents a 2-thienylcarbonyl group;
the chemical formula (16):

[0185]

20 [Chemical Formula 183]



[0186]

represents a group of substituted or non-substituted phenylsulfinyl groups in which R₁₂ represents a

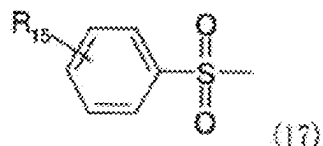
5 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₃ group, a SO₂R₁₄ group (R₁₃ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₄ represents either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a

10 C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₂ may be the same or different for each unit;

the chemical formula (17):

[0187]

15 [Chemical Formula 184]



[0188]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R₁₅ represents a

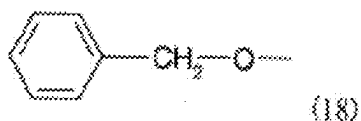
20 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆ group, a SO₂R₁₇ group (R₁₆ represents either one of H, Na, K, CH₃ and C₂H₅; and R₁₇ represents either one of OH,

ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₁₅ may be the same or different for each unit;

5 the chemical formula (18):

[0189]

[Chemical Formula 185]



[0190]

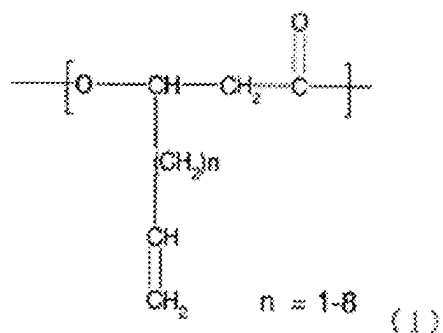
10 represents a (phenylmethyl)oxy group.

[0191]

[19] The method according to [17] or [18], wherein the starting material polyhydroxy alkanoate copolymer including at least a 3-hydroxy- ω -alkenoic acid unit represented by a chemical formula (1) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule, 15 is produced by a method according to any one of [8] to [16];

[0192]

[Chemical Formula 186]

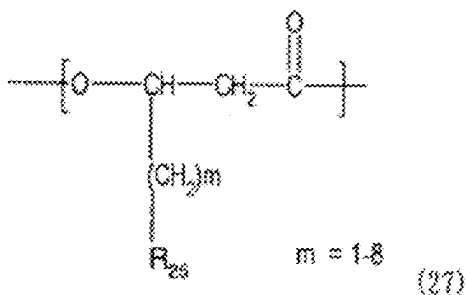


[0193]

in which n represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, n may be the same or different for each unit;

[0194]

[Chemical Formula 187]

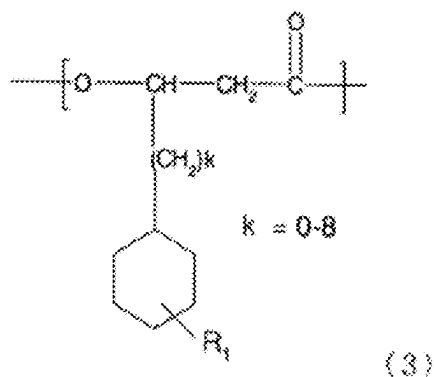


10 [0195]

in which m represents an integer selected within a range indicated in the chemical formula; R₂₅ represents a residue having any of a phenyl structure or a thienyl structure; and in case plural units are present, m and R₂₅ may be the same or different for each unit; and

[0196]

[Chemical Formula 188]



[0197]

in which R_1 represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R_1 may be the same or different for each unit.

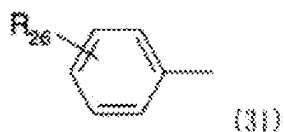
[20] The method for producing a polyhydroxy alkanate copolymer according to [19], wherein R_{25} in the chemical formula (27), representing a residue having a phenyl structure or a thienyl structure, is at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0198]

the chemical formula (31):

[0199]

[Chemical Formula 189]



[0200]

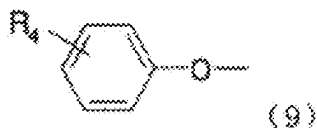
(31)

represents a group of substituted or non-substituted
 5 phenyl groups in which R_{26} represents a substituent on
 an aromatic ring and represents an H atom, a halogen
 atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
 a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group
 or a C_3F_7 group; and in case plural units are present,
 10 R_{26} may be the same or different for each unit;

the chemical formula (9):

[0201]

[Chemical Formula 190]



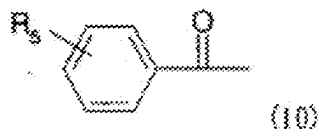
15 [0202]

represents a group of non-substituted or substituted
 phenoxy groups in which R_4 represents a substituent on
 an aromatic ring and represents an H atom, a halogen
 atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
 20 a C_3H_7 group, a SCH_3 group, a CF_3 group, a C_2F_5 group, or
 a C_3F_7 group; and in case plural units are present, R_4
 may be the same or different for each unit;

the chemical formula (10):

[0203]

[Chemical Formula 191]



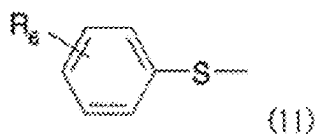
[0204]

represents a group of non-substituted or substituted
5 benzoyl groups in which R_5 represents a substituent on
an aromatic ring and represents an H atom, a halogen
atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group,
a C_3H_7 group, a CF_3 group, a C_2F_5 group, or a C_3F_7 group;
and in case plural units are present, R_5 may be the
10 same or different for each unit;

the chemical formula (11):

[0205]

[Chemical Formula 192]



15 [0206]

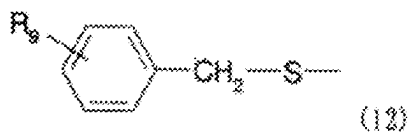
represents a group of substituted or non-substituted
phenylsulfanyl groups in which R_6 represents a
substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO_2 group, a $COOR_7$
20 group, a SO_2R_8 group (R_7 representing either one of H,
Na, K, CH_3 and C_2H_5 ; and R_8 representing either one of
OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3
group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a

(CH₃)₃-C group; and in case plural units are present, R₆ may be the same or different for each unit;

the chemical formula (12):

[0207]

5 [Chemical Formula 193]



[0208]

represents a group of substituted or non-substituted (phenylmethyl)sulfanyl groups in which R₉ represents a
10 substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀ group, a SO₂R₁₁ group (R₁₀ representing either one of H, Na, K, CH₃ and C₂H₅; and R₁₁ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃
15 group, a C₂H₅ group, a C₃H⁷ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₉ may be the same or different for each unit;

the chemical formula (13):

[0209]

20 [Chemical Formula 194]



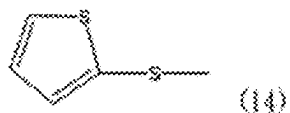
[0210]

represents a 2-thienyl group;

the chemical formula (14):

[0211]

[Chemical Formula 195]



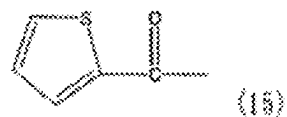
5 [0212]

represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0213]

[Chemical Formula 196]



10

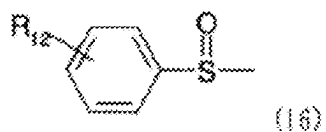
[0214]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0215]

15 [Chemical Formula 197]



[0216]

represents a group of substituted or non-substituted
phenylsulfinyl groups in which R₁₂ represents a
20 substituent on an aromatic ring and represents an H
atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₃
group, a SO₂R₁₄ group (R₁₃ representing either one of H,

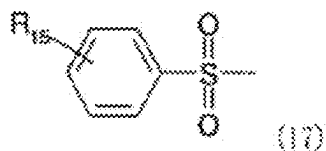
Na, K, CH₃ and C₂H₅; and R₁₄ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present,

5 R₁₂ may be the same or different for each unit;

the chemical formula (17):

[0217]

[Chemical Formula 198]



10 [0218]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R₁₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₆

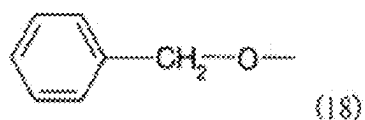
15 group, a SO₂R₁₇ group (R₁₆ representing either one of H, Na, K, CH₃ and C₂H₅; and R₁₇ representing either one of OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present,

20 R₁₅ may be the same or different for each unit; and

the chemical formula (18):

[0219]

[Chemical Formula 199]



[0220]

represents a (phenylmethyl)oxy group.

[0221]

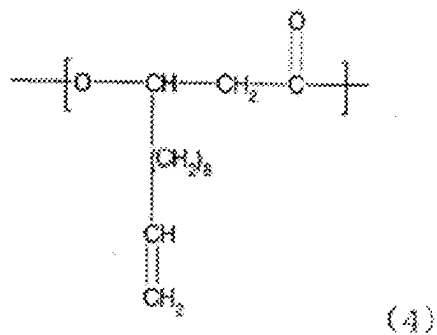
- 5 [21] The polyhydroxy alkanooate copolymer according to any one of [17] to [20], wherein the 3-hydroxy- ω -alkenoic acid unit represented by the chemical formula (1) is any one of

[0222]

- 10 a 3-hydroxy-12-tridecenoic acid unit represented by a chemical formula (4):

[0223]

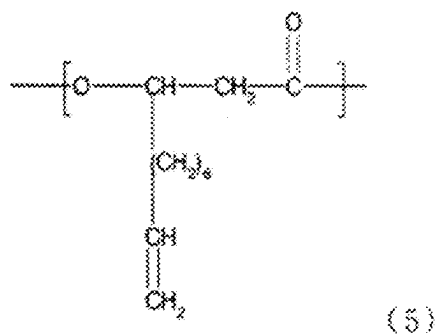
[Chemical Formula 200]



- 15 [0224] a 3-hydroxy-10-undecenoic acid unit represented by a chemical formula (5):

[0225]

[Chemical Formula 201]

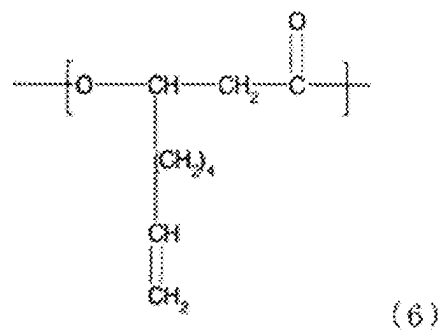


[0226]

a 3-hydroxy-8-nonenoic acid unit represented by a chemical formula (6): and

5 [0227]

[Chemical Formula 202]



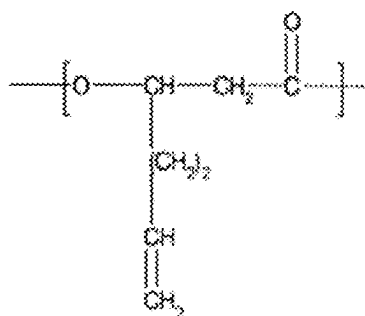
[0228]

a 3-hydroxy-6-heptenoic acid unit represented by a chemical formula (7)

10

[0229]

[Chemical Formula 203]



(7).

[0230]

[22] The producing method according to any one of [17] to [21], wherein the oxidation and cleavage
5 reaction is carried out with an oxidant selected from a group consisting of a permanganate, a bichromate and a periodate.

[0231]

[23] The producing method according to [22],
10 wherein the oxidation and cleavage reaction is carried out with a permanganate as an oxidant and under an acidic condition.

[0232]

[24] The producing method according to any one of
15 [17] to [21], wherein the oxidation and cleavage reaction is carried out with ozone.

[0233]

[25] A method for producing a polyhydroxy
alkanoate copolymer, characterized in employing a
20 polyhydroxy alkanoate copolymer including at least a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit represented

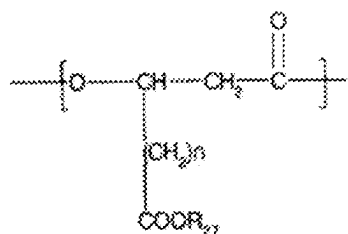
by a chemical formula (32) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a chemical formula (27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a
5 chemical formula (3) in the molecule as a starting material,

and executing a hydrolysis in the presence of an acid or an alkali or executing a hydrogenolysis including a catalytic reduction,

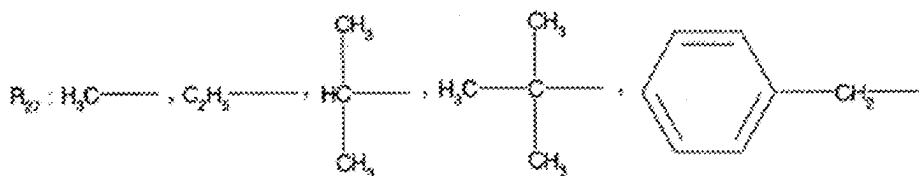
10 thereby generating a polyhydroxy alkanoate copolymer including at least a 3-hydroxy- ω -carboxyalkanoic acid unit represented by a chemical formula (19) in a molecule, and simultaneously at least a 3-hydroxy- ω -alkanoic acid unit represented by a
15 chemical formula (27) or a 3-hydroxy- ω -cyclohexylalkanoic acid unit represented by a chemical formula (3) in the molecule:

[0234]

[Chemical Formula 204]



$n = 1-8 \quad (32)$

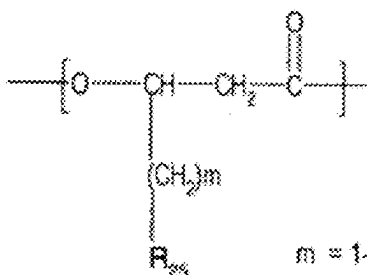


[0235]

in which n represents an integer selected within a range indicated in the chemical formula; R₂₇ represents
 5 any of residues indicated in the chemical formula; and in case plural units are present, n and R₂₇ may be the same or different for each unit;

[0236]

[Chemical Formula 205]



$m = 1-8 \quad (27)$

10

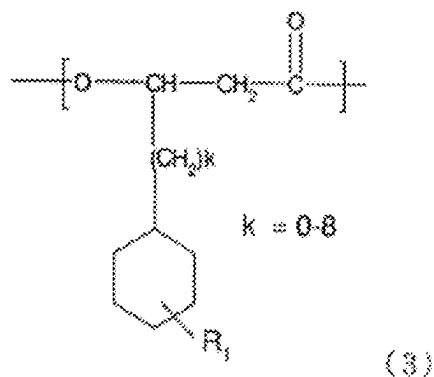
[0237]

in which m represents an integer selected within a range indicated in the chemical formula; R₂₅ includes a

residue having any of a phenyl structure and a thienyl structure; and in case plural units are present, m and R₂₅ may be the same or different for each unit;

[0238]

5 [Chemical Formula 206]

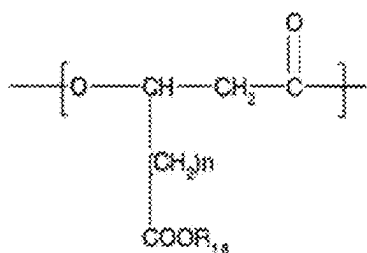


[0239]

in which R₁ represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; k represents an integer selected within a range indicated in the chemical formula; and in case plural units are present, R₁ may be the same or different for each unit; and

15 [0240]

[Chemical Formula 207]



$$n = 1-8 \quad (19)$$

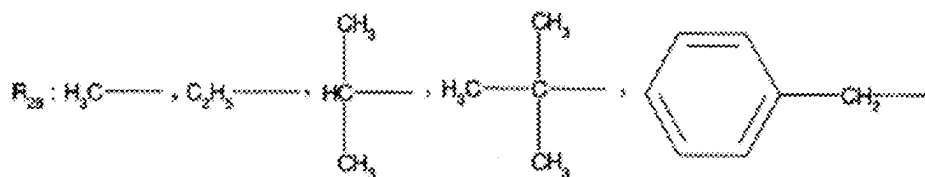
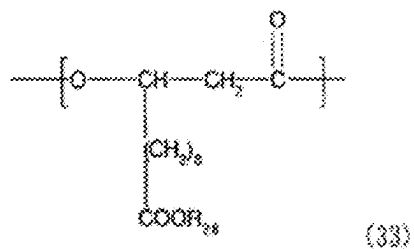
[0241]

in which n represents an integer selected within a range indicated in the chemical formula; R₁₈ represents
 5 an H atom, a Na atom, or a K atom; and in case plural units are present, n and R₁₈ may be the same or different for each unit.

[26] The polyhydroxy alkanoate copolymer according to [25], wherein the 3-hydroxy-ω-
 10 alkoxy-carbonylalkanoic acid unit represented by the chemical formula (32) is any one of a 3-hydroxy-11-alkoxy-carbonylundecanoic acid unit represented by a chemical formula (33):

[0242]

15 [Chemical Formula 208]



[0243]

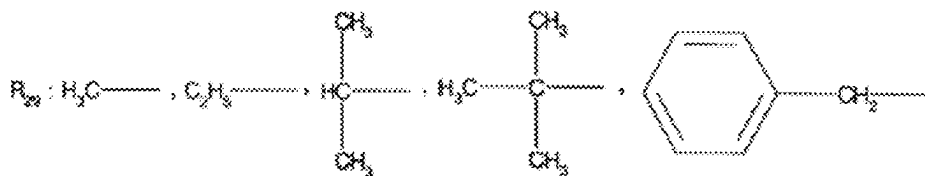
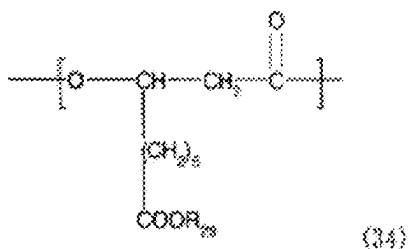
(R₂₈ represents any of residues indicated in the chemical formula; and in case plural units are present,

5 R₂₈ may be the same or different for each unit),

a 3-hydroxy-9-alkoxycarboxynonanoic acid unit represented by a chemical formula (34):

[0244]

[Chemical Formula 209]



10

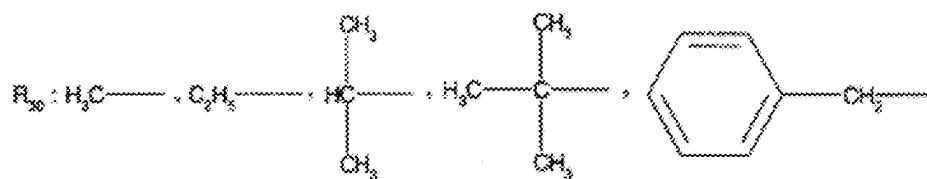
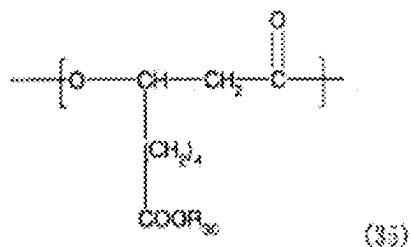
[0245]

(R₂₉ represents any of residues indicated in the

chemical formula; and in case plural units are present,
 R_{29} may be the same or different for each unit),
 a 3-hydroxy-7-alkoxycarboxyheptanoic acid unit
 represented by a chemical formula (35):

5 [0246]

[Chemical Formula 210]

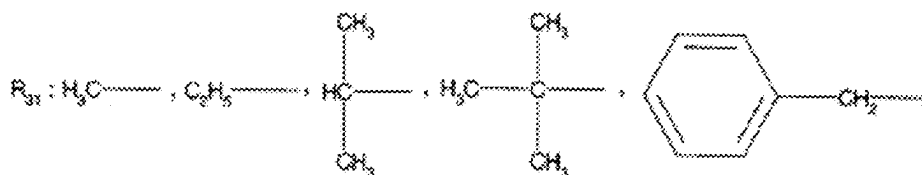
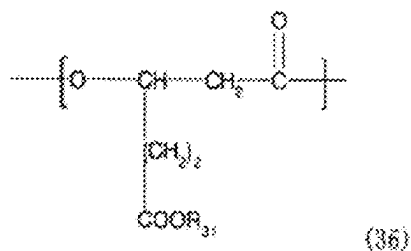


[0247]

(R_{30} represents any of residues indicated in the
 10 chemical formula; and in case plural units are present,
 R_{30} may be the same or different for each unit), and
 a 3-hydroxy-5-alkoxycarboxyvaleric acid unit
 represented by a chemical formula (36):

[0248]

15 [Chemical Formula 211]



[0249]

(R₃₁ represents any of residues indicated in the chemical formula; and in case plural units are present,

5 R₃₁ may be the same or different for each unit).

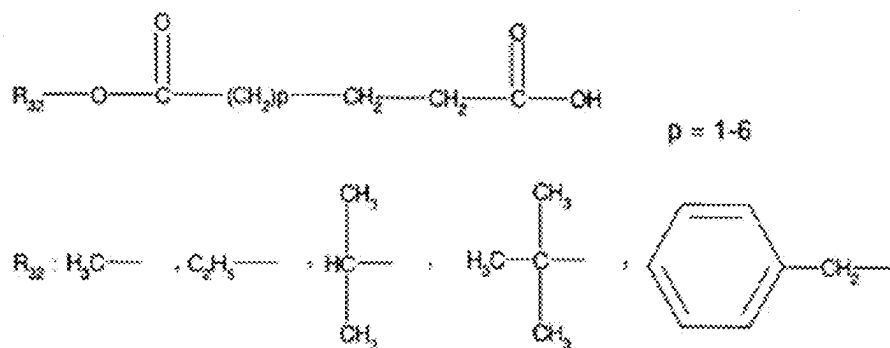
[0250]

[27] The method for producing a polyhydroxy
alkanoate copolymer including the 3-hydroxy- ω -
carboxyalkanoic acid according to [25] or [26] hydro-
10 synthesized by a microorganism having an ability of
producing a polyhydroxy alkanoate copolymer including
at least a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit
represented by a chemical formula (32) in a molecule,
and simultaneously at least a 3-hydroxy- ω -alkanoic acid
15 unit represented by a chemical formula (27) or a 3-
hydroxy- ω -cyclohexylalkanoic acid unit represented by a
chemical formula (3) in the molecule,

from a dicarboxylic acid monoester compound
represented by a chemical formula (37):

[0251]

[Chemical Formula 212]



(37)

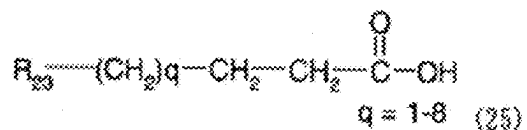
5 [0252]

in which p represents an integer selected within a range indicated in the chemical formula; and R_{32} represents any of residues indicated in the chemical formula;

10 and at least a compound represented by a chemical formula (25) or at least a ω -cyclohexylalkanoic acid represented by a chemical formula (26) as starting materials:

[0253]

15 [Chemical Formula 213]



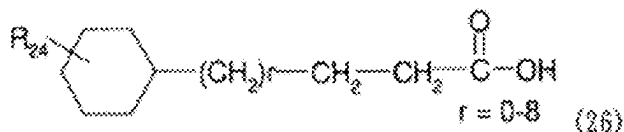
[0254]

in which q represents an integer selected within a range indicated in the chemical formula; and R_{23}

includes a residue having a phenyl structure or a thienyl structure;

[0255]

[Chemical Formula 214]



5

[0256]

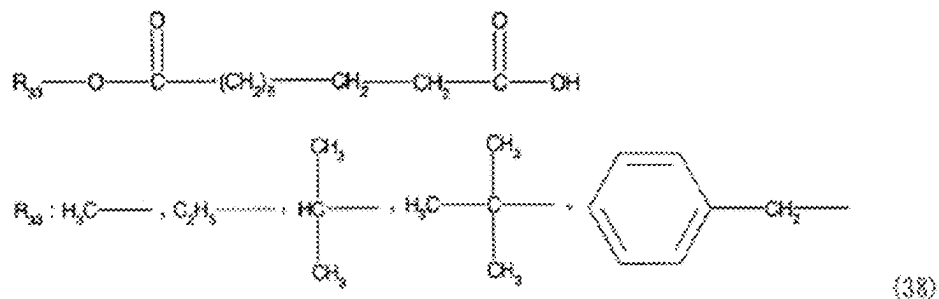
in which R₂₄ represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and r represents an integer selected within a range indicated in the chemical formula.

[28] The polyhydroxy alkanooate copolymer according to [27], wherein the dicarboxylic acid monoester compound represented by the chemical formula (37) is any one of a sebacic acid monoester compound represented by a chemical formula (38):

15

[0257]

[Chemical Formula 215]



20

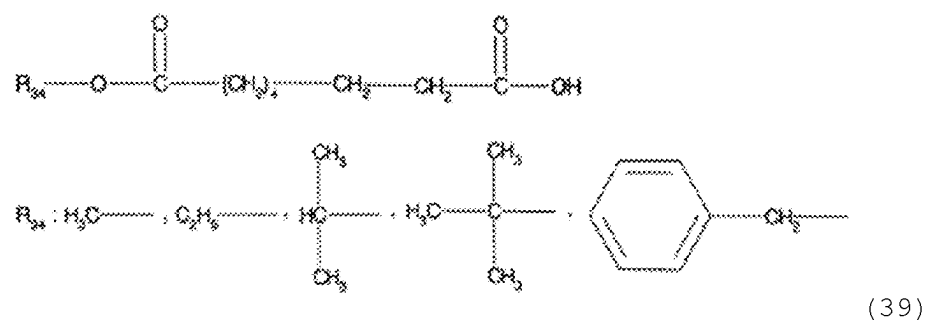
[0258]

(R₃₃ represents any of residues indicated in the chemical formula), or

a suberic acid monoester compound represented by a
5 chemical formula (39):

[0259]

[Chemical Formula 216]

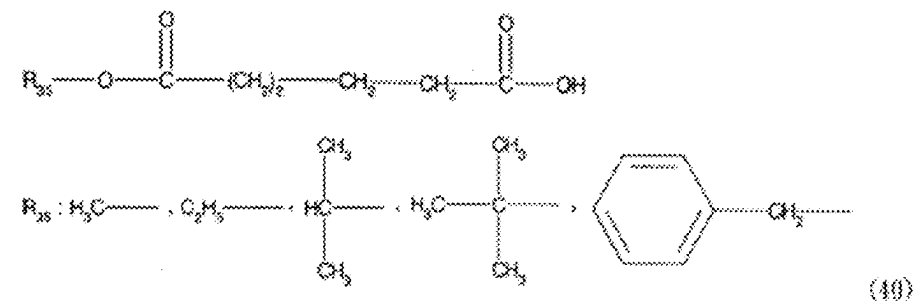


[0260]

10 (R₃₄ represents any of residues indicated in the chemical formula), or
a adipic acid monoester compound represented by a
chemical formula (37):

[0261]

15 [Chemical Formula 217]



[0262]

(R₃₅ represents any of residues indicated in the chemical formula).

[0263]

[29] The method for producing a polyhydroxy
5 alkanooate copolymer including at least the 3-hydroxy- ω -
carboxyalkanoic acid according to [27] or [28] in a
molecule, which hydro-synthesizes a 3-hydroxy- ω -
alkoxycarbonylalkanoic acid unit represented by the
chemical formula (32) by cultivating a microorganism in
10 a culture medium including at least a dicarboxylic acid
monoester compound represented by a chemical formula
(37), and at least a compound represented by the
chemical formula (25) or at least a ω -
cyclohexylalkanoic acid represented by a chemical
15 formula (26).

[0264]

[30] The method for producing a polyhydroxy
alkanoate copolymer according to [29], wherein the
microorganism is cultured in a culture medium including,
20 in addition to at least a dicarboxylic acid monoester
compound represented by the chemical formula (37), and
at least a compound represented by the chemical formula
(25) or at least a ω -cyclohexylalkanoic acid
represented by the chemical formula (26), at least one
25 of a peptide, an yeast extract, an organic acid or a
salt thereof, an amino acid or a salt thereof, a sugar,
a linear alkanoic acid with 4 to 12 carbon atoms or a

salt thereof.

[0265]

[31] The method for producing a polyhydroxy
alkanoate copolymer according to [30], wherein for
5 culturing the organism, the peptide to be added to the
culture medium is polypeptone; organic acid or salt
thereof to be added to the culture medium is one or
more compound selected from a group of piruvic acid,
oxaloacetic acid, citric acid, isocitric acid,
10 ketoglutaric acid, succinic acid, fumaric acid, malic
acid, lactic acid and salts thereof; amino acid or salt
thereof to be added to the culture medium is one or
more compound selected from a group of glutamic acid,
aspartic acid and salts thereof; and sugar to be added
15 to the culture medium is one or more compound selected
from a group of glyceraldehyde, erythrose, arabinose,
xylose, glucose, galactose, mannose, fructose, glycerol,
erythritol, xylitol, gluconic acid, glucuronic acid,
galacturonic acid, maltose, sucrose and lactose.

20 [0266]

[32] The method for producing a polyhydroxy
alkanoate copolymer according to any one of [27] to
[31], characterized in including a step of culturing
the microorganism in a culture medium including at
25 least a dicarboxylic acid monoester compound
represented by the chemical formula (37) and at least a
compound represented by the chemical formula (25) or at

least an ω -cyclohexylalkanoic acid represented by the
chemical formula (26), and recovering a polyhydroxy
alkanoate copolymer including simultaneously at least a
3-hydroxy- ω -alkoxycarbonylalkanoic acid unit
5 represented by the chemical formula (32) and a 3-
hydroxy- ω -alkanoic acid unit represented by the
chemical formula (2) or a 3-hydroxy- ω -
cyclohexylalkanoic acid unit represented by the
chemical formula (3) in the molecule, produced by the
10 microorganism, from cells of the microorganism.
[0267]

[33] The method for producing a polyhydroxy
alkanoate copolymer according to [27] to [32], wherein
the microorganism is a microorganism belonging to
15 *Pseudomonas* genus.
[0268]

[34] The method for producing a polyhydroxy
alkanoate copolymer according to [33], wherein the
microorganism is at least one of *Pseudomonas cichorii*
20 YN2 strain (FERM BP-7375), *Pseudomonas cichorii* H45
strain (FERM BP-7374), *Pseudomonas jessenii* P161 (FERM
BP-7376) and *Pseudomonas putida* P91 (FERM BP-7373).
[0269]

[35] The method for producing a polyhydroxy
25 alkanoate copolymer according to [25] to [34], wherein
 R_{25} in the chemical formula (27) and R_{23} in the chemical
formula (25), each representing a residue having a

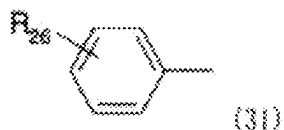
phenyl structure or a thienyl structure, represents at least one of chemical formulas (31), (9), (10), (11), (12), (13), (14), (15), (16), (17) and (18):

[0270]

5 the chemical formula (31):

[0271]

[Chemical Formula 218]



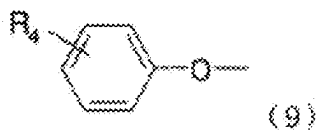
[0272]

10 represents a group of substituted or non-substituted phenyl groups in which R_{26} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $CH=CH_2$ group, a CF_3 group, a C_2F_5 group
15 or a C_3F_7 group; and in case plural units are present, R_{26} may be the same or different for each unit;

the chemical formula (9):

[0273]

[Chemical Formula 219]



20

[0274]

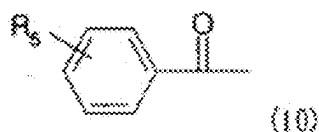
represents a group of non-substituted or substituted phenoxy groups in which R_4 represents a substituent on an aromatic ring and represents an H atom, a halogen

atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a SCH₃ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and in case plural units are present, R₄ may be the same or different for each unit;

5 the chemical formula (10):

[0275]

[Chemical Formula 220]



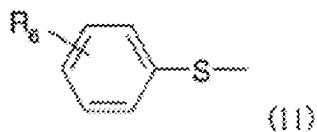
[0276]

10 represents a group of non-substituted or substituted benzoyl groups in which R₅ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group;
15 and in case plural units are present, R₅ may be the same or different for each unit;

the chemical formula (11):

[0277]

[Chemical Formula 221]



20

[0278]

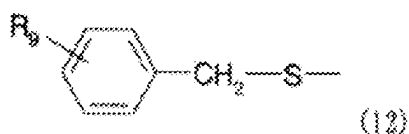
represents a group of substituted or non-substituted phenylsulfanyl groups in which R₆ represents a

substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₇ group, a SO₂R₈ group (R₇ representing either one of H, Na, K, CH₃ and C₂H₅; and R₈ representing either one of
 5 OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₆ may be the same or different for each unit;

the chemical formula (12):

10 [0279]

[Chemical Formula 222]



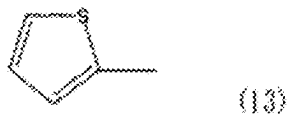
[0280]

represents a group of substituted or non-substituted
 15 (phenylmethyl)sulfanyl groups in which R₉ represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO₂ group, a COOR₁₀ group, a SO₂R₁₁ group (R₁₀ representing either one of H, Na, K, CH₃ and C₂H₅; and R₁₁ representing either one of
 20 OH, ONa, OK, a halogen atom, OCH₃ and OC₂H₅), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and in case plural units are present, R₉ may be the same or different for each unit;

the chemical formula (13):

25 [0281]

[Chemical Formula 223]



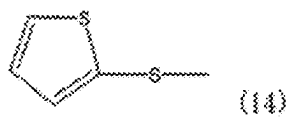
[0282]

represents a 2-thienyl group;

5 the chemical formula (14):

[0283]

[Chemical Formula 224]



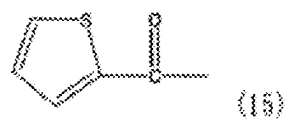
[0284]

10 represents a 2-thienylsulfanyl group;

the chemical formula (15):

[0285]

[Chemical Formula 225]



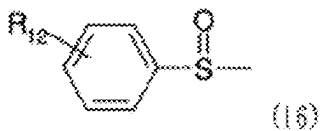
15 [0286]

represents a 2-thienylcarbonyl group;

the chemical formula (16):

[0287]

[Chemical Formula 226]



20

[0288]

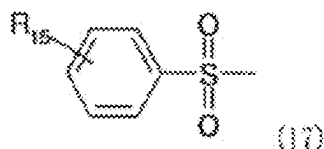
represents a group of substituted or non-substituted phenylsulfinyl groups in which R_{12} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{13}$ group, a SO_2R_{14} group (R_{13} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{14} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present,

10 R_{12} may be the same or different for each unit;

the chemical formula (17):

[0289]

[Chemical Formula 227]



15 [0290]

represents a group of substituted or non-substituted phenylsulfonyl groups in which R_{15} represents a substituent on an aromatic ring and represents an H atom, a halogen atom, a CN group, a NO_2 group, a $COOR_{16}$ group, a SO_2R_{17} group (R_{16} representing either one of H, Na, K, CH_3 and C_2H_5 ; and R_{17} representing either one of OH, ONa, OK, a halogen atom, OCH_3 and OC_2H_5), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and in case plural units are present,

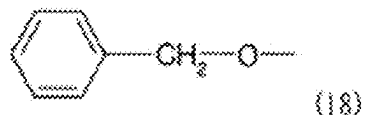
20 R_{15} may be the same or different for each unit; and

25

the chemical formula (18):

[0291]

[Chemical Formula 228]



5 [0292]

represents a (phenylmethyl)oxy group.

[0293]

The contents of the present invention will be described in details hereinafter.

10 [0294]

[Embodiment(s)]

A polyhydroxy alkanoate copolymer, the final product of the present invention, is a polyhydroxy alkanoate copolymer (hereinafter also called carboxyl
15 PHA) comprising a unit having a carboxyl group on a side chain as represented by a chemical formula (19) and a unit represented by a chemical formula (2) or a chemical formula (3).

[0295]

20 The producing methods therefor are mainly classified to:

- a method of oxidizing and cleaving a double bond portion in a polyhydroxy alkanoate copolymer (hereinafter also called a precursor vinyl PHA)
25 including a 3-hydroxy- ω -alkenoic acid unit having a carbon-carbon double bond at an end of a side chain as

represented in a chemical formula (1) and a unit represented by a chemical formula (2) or a chemical formula (3); and

- a method of hydrolyzing an alkoxycarbonyl portion in a polyhydroxy alkanate copolymer (hereinafter also called an alkoxycarbonyl PHA) including a 3-hydroxy- ω -alkoxyalkanoic acid unit having an ester group at an end of a side chain as represented in a chemical formula (32) and a unit represented by a chemical formula (2) or a chemical formula (3). In the following, the precursor vinyl PHA and the precursor alkoxycarbonyl PHA may be collectively called a precursor PHA.

[0296]

- 15 A producing method for such precursor PHA is not particularly restricted, but there can be employed a microbial production using microorganisms, a method using a genetically modified plant, or a chemical polymerization. Preferably a method by microbial production is employed.

[0297]

- 25 The precursor vinyl PHA was synthesized for the first time by the present inventors, and the present invention therefore includes also the precursor vinyl PHA itself, and a production process thereof by microorganisms. Also such precursor vinyl PHA can be effectively utilized not only for the carboxyl PHA

which is an object of the present invention but also
for introducing other functional groups.

[0298]

In the following, there will be explained a
5 producing method employing each precursor PHA.

[0299]

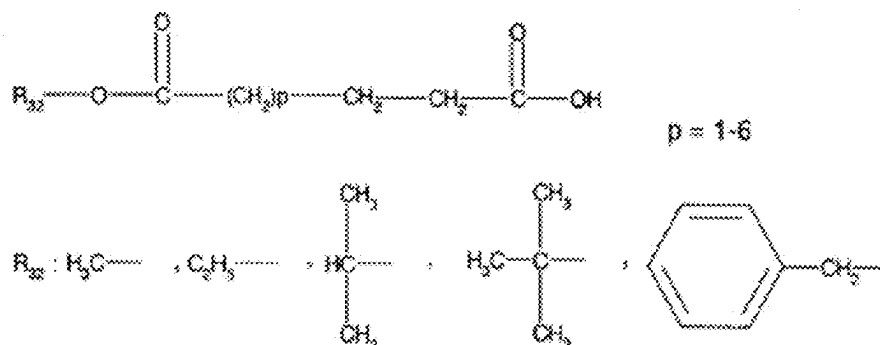
The precursor vinyl PHA can be producing by
culturing a microorganism in a culture medium including
an ω -alkenoic acid represented by a chemical formula
10 (24) and a compound represented by a chemical formula
(25) or an ω -cyclohexylalkanoic acid represented by the
chemical formula (26).

[0300]

Similarly, the precursor alkoxycarbonyl PHA can be
15 producing by culturing a microorganism in a culture
medium including a carboxylic acid monoester compound
represented by a chemical formula (37) and a compound
represented by the chemical formula (25) or an ω -
cyclohexylalkanoic acid represented by the chemical
20 formula (26).

[0301]

[Chemical Formula 229]



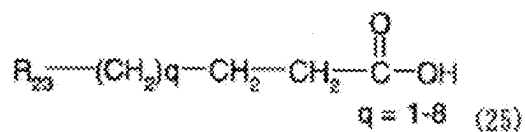
(37)

[0302]

in which p represents an integer selected within a
 5 range indicated in the chemical formula; and R_{32}
 represents any of residues indicated in the chemical
 formula;

[0303]

[Chemical Formula 230]



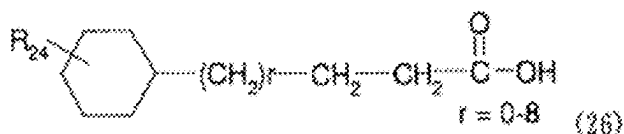
10

[0304]

in which q represents an integer selected within a
 range indicated in the chemical formula; and R_{23}
 includes a residue having a phenyl structure or a
 15 thienyl structure;

[0305]

[Chemical Formula 231]



[0306]

in which R₂₄ represents a substituent on a cyclohexyl group and represents an H atom, a CN group, a NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group, or a C₃F₇ group; and r represents an integer selected within a range indicated in the chemical formula.

More specifically, each precursor PHA can be more advantageously prepared by culturing a microorganism in a culture medium containing respective raw material compounds, namely, for the precursor vinyl PHA, a combination of at least one ω-alkenoic acid represented by the chemical formula (24) and at least one compound represented by the chemical formula (25) or at least one ω-cyclohexylalkanoic acid represented by the chemical formula (26); and for the precursor alkoxy carbonyl PHA, a combination of at least one carboxylic acid monoester compound represented by the chemical formula (37) and at least one compound represented by the chemical formula (25) or at least one ω-cyclohexylalkanoic acid represented by the chemical formula (26), and further containing at least one of peptide, yeast extract, organic acid or salt thereof, amino acid or a salt thereof, sugar, and

linear alkanolic acid with 4 to 12 carbon atoms or salt thereof.

[0307]

As preferable nutrients to be added to the culture
5 medium, the peptide being polypeptone; one or more
organic acids selected from a group of piruvic acid,
oxaloacetic acid, citric acid, isocitric acid,
ketoglutaric acid, succinic acid, fumaric acid, malic
acid, lactic acid and salts thereof; one or more amino
10 acids selected from a group of glutamic acid, aspartic
acid and salts thereof; and one or more sugars selected
from a group of glyceraldehyde, erythrose, arabinose,
xylose, glucose, galactose, mannose, fructose, glycerol,
erythritol, xylitol, gluconic acid, glucuronic acid,
15 galacturonic acid, maltose, sucrose and lactose.

[0308]

In the producing method of the precursor PHA
copolymer of the present invention, detailed microbial
culture conditions are as follows.

20 [0309]

The following necessary substrates and nutrients
are added to an inorganic salt culture medium based on
a phosphate buffer and an ammonium salt or a nitrate
salt.

25 [0310]

The raw material compound for each precursor PHA,
namely, for the precursor vinyl PHA, a combination of

at least an ω -alkenoic acid represented by the chemical
formula (24) and at least a compound represented by the
chemical formula (25) or at least an ω -
cyclohexylalkanoic acid represented by the chemical
5 formula (26); or for the precursor alkoxycarbonyl PHA,
a combination of at least a carboxylic acid monoester
compound represented by the chemical formula (37) and
at least a compound represented by the chemical formula
(25) or at least an ω -cyclohexylalkanoic acid
10 represented by the chemical formula (26), is preferably
contained in the culture medium in a proportion of 0.01
to 1 % (w/v), further preferably 0.02 to 0.2 %.
[0311]

The aforementioned nutrients as a carbon source
15 and a nitrogen source for proliferation, and as an
energy source for polyhydroxy alkanoate production are
preferably added to the culture medium in a proportion
of 0.1 to 5 % (v/v) per medium, more preferably 0.2 to
2 %.
20 [0312]

It can be employed any inorganic salt culture
medium containing a phosphate salt and a nitrogen
source such as an ammonium salt or a nitrate salt, but
the PHA productivity can be improved by regulating the
25 concentration of the nitrogen source.
[0313]

The culture temperature can be any temperature at

which the microorganism can satisfactorily proliferate, and is usually within a range of 15 to 37°C, preferably 20 to 30°C.

[0314]

5 The culture may be carried out by any culture method so long as the microorganisms can proliferate and produce PHA, such as a liquid culture or a solid culture. Also it may be batch culture, fed batch culture, semi-continuous culture or continuous culture.

10 For example, for liquid batch culture, the oxygen supply method may be shaking using a shaking flask or agitation aeration in a jar fermenter.

[0315]

 In order to make the microorganism produce and
15 accumulate PHA, there can be employed, in addition to the aforementioned method, a method of transferring the cell, after sufficient proliferation, to a culture medium limited in a nitrogen source such as ammonium chloride and to continue culture further in the
20 presence of a compound being a substrate for the desired unit, thereby improving the productivity.

[0316]

 Thus the method for producing precursor vinyl PHA of the present invention may comprise the steps of:
25 culturing a production microorganism under the aforementioned conditions, and recovering produced PHA from the cells, the PHA copolymer produced by the

microorganism at least containing a 3-hydroxy- ω -
alkenoic acid unit represented by the chemical formula
(1), and a unit represented by the chemical formula (2)
or an ω -cyclohexylalkanoic acid unit represented by the
5 chemical formula (3) in the molecule.

[0317]

Also the method for producing precursor
alkoxycarbonyl PHA of the present invention may
comprise the steps of: culturing a production
10 microorganism under the aforementioned conditions, and
recovering from the cells a polyhydroxy alkanoate
copolymer produced by the microorganism which at least
contains a 3-hydroxy- ω -alkoxycarbonylalkanoic acid unit
represented by the chemical formula (32), and a unit
15 represented by the chemical formula (2) or an ω -
cyclohexylalkanoic acid unit represented by the
chemical formula (3) in the molecule.

[0318]

The object PHA can be recovered from the cells by
20 an ordinarily employed method. For example, an
extraction with an organic solvent such as chloroform,
dichloromethane or acetone is most simple, but there
may also be employed dioxane, tetrahydrofuran or
acetonitrile. Also in a situation where an organic
25 solvent is difficult to use, it is also possible to
physically break the cells, for example by treating the
cells with a surfactant such as SDS, chemicals such as

hypochlorous acid and EDTA, or with an enzyme such as lysozyme, or by ultrasonic disruption, homogenizer disruption, pressure disruption, beads impulse, grinding or pounding or freeze-and-thawing, to remove
5 cell components other than PHA and recover PHA.

[0319]

A production microorganism to be employed in the production method of the present invention can be any microorganisms having an ability meeting the
10 aforementioned conditions, but there are preferred those belonging to the *Pseudomonas* genus, and more preferably *Pseudomonas cichorii*, *Pseudomonas putida*, *Pseudomonas fluorescense*, *Pseudomonas oleovorans*, *Pseudomonas aeruginosa*, *Pseudomonas stutzeri* or
15 *Pseudomonas jessenii*. More specific examples include *Pseudomonas cichorii* YN2 (FERM BP-7375), *Pseudomonas cichorii* H45 (FERM BP-7374), *Pseudomonas jessenii* P161 (FERM BP-7376), and *Pseudomonas putida* P91 (FERM BP-7373). These four types of strains are deposited on
20 November 20, 2000 at International Patent Organism Depositary, National Institute of Bioscience and Human-Technology, Agency of Industry Science and Technology (independent administrative corporation), Tsukuba Central 6, 1-1, Higashi 1-chome, Tsukuba-shi, Ibaraki-
25 ken 305-8566, Japan, and described in the Japanese Patent Application Laid-Open No. 2002-80571.

[0320]

In the present invention the methods for culture of the microorganism, PHA production and accumulation by the microorganism, and for PHA recovery from the cells are not limited to the methods explained above.

5 [0321]

The following is a composition of an inorganic salt M9 culture medium employed in the method of the present invention.

[0322]

10 [M9 culture medium]

Na₂HPO₄ 6.3

KH₂PO₄ 3.0

NH₄Cl 1.0

NaCl 0.5

15 (in g/L; pH 7.0)

[0323]

For satisfactory proliferation and resulting PHA production, the above-mentioned inorganic culture medium has to be replenished with the essential trace
20 elements by adding the following trace component solution by about 0.3 % (v/v).

[0324]

[Minor component solution]

Nytrilotriacetic acid 1.5;

25 MgSO₄ 3.0;

MnSO₄ 0.5;

NaCl 1.0;

	FeSO ₄	0.1;
	CaCl ₂	0.1;
	CoCl ₂	0.1;
	ZnSO ₄	0.1;
5	CuSO ₄	0.1;
	AlK(SO ₄) ₂	0.1;
	H ₃ BO ₃	0.1;
	Na ₂ MoO ₄	0.1;
	NiCl ₂	0.1;
10	(in g/L).	
	[0325]	

The polyhydroxy alkanoates synthesized by the
aforementioned producing method, a polyhydroxy
alkanoate copolymer including a unit represented by the
15 chemical formula (1) and a unit represented by the
chemical formula (2) or a unit represented by the
chemical formula (3) can be oxidized at the carbon-
carbon double bond portion to give a polyhydroxy
alkanoate copolymer including a unit represented by the
20 chemical formula (19), and a unit represented by the
chemical formula (2) or a unit represented by the
chemical formula (3). For obtaining a carboxylic acid
by oxidizing a carbon-carbon double bond with an
oxidant, there are known, for example, a method of
25 utilizing a permanganate salt (J. Chem. Soc. Perkin.
Trans. 1, 806 (1973); Non-patent Document 16)); a
method of utilizing a bichromate salt (Org. Synth., 4,

698 (1963); Non-patent Document 17); a method of
utilizing a periodate salt (J. Org. Chem., 46, 19
(1981); Non-patent Document 18); a method of utilizing
nitric acid (Japanese Patent Application Laid-Open No.
5 S59-190945; Patent Document 9); a method of utilizing
ozone (J. Am. Chem. Soc., 81, 4273 (1959); Non-patent
Document 19) etc., and, on polyhydroxy alkanoate,
Macromolecular chemistry, 4, 289-293 (2001) (Non-patent
Document 14) reports a method of obtaining a carboxylic
10 acid by oxidizing the carbon-carbon double bond at the
end of the side chain of polyhydroxy alkanoate with
potassium permanganate as an oxidant and under an
acidic condition. A similar method can be utilized
also in the present invention.

15 [0326]

The oxidant to be employed in the present
invention, though not particularly limited, is
preferably a permanganate salt. Such permanganate salt
to be employed as the oxidant is usually potassium
20 permanganate. Since the oxidation reaction is a
stoichiometric reaction, the amount of the permanganate
salt is usually 1 molar equivalent or more with respect
to 1 mole of the unit represented by the chemical
formula (1), preferably 2 to 10 molar equivalents.

25 [0327]

For executing the reaction under an acidic
condition, there is usually employed an inorganic acid

such as sulfuric acid, hydrochloric acid, acetic acid or nitric acid, or an organic acid. However the use of sulfuric acid, nitric acid or hydrochloric acid may cause cleavage of an ester bond in the main chain of polyhydroxy alkanoate, thereby resulting in a decrease in the molecular weight. It is therefore preferable to employ acetic acid. An amount of acid is usually within a range of 0.2 to 200 molar equivalents per 1 mole of the unit represented by the chemical formula (1), preferably 0.4 to 100 molar equivalents. An amount less than 0.2 molar equivalents results in a low yield, while an amount exceeding 200 molar equivalents generates by-products by decomposition with acid. Also a crown ether may be employed for the purpose of accelerating the reaction. In this case, crown ether and permanganate salt form a complex, thereby providing an effect of increasing the reaction activity. As the crown ether, there is generally employed dibenzo-18-crown-6-ether, dicyclo-18-crown-6-ether, or 18-crown-6-ether. An amount of crown ether is generally within a range of 0.5 to 2.0 molar equivalents per 1 mole of permanganate salt, preferably 0.5 to 1.5 molar equivalents.

[0328]

As a solvent to be employed in the oxidation and cleavage reaction of the present invention, there may be employed any solvent inert to the reaction without

particular limitation, for example water, acetone; an ether such as tetrahydrofuran or dioxane; an aromatic hydrocarbon such as benzene; an aliphatic hydrocarbon such as hexane or heptane; or a halogenated hydrocarbon
5 such as methyl chloride, dichloromethane or chloroform. Among these solvents, in consideration of dissolving property for polyhydroxy alkanoate, a halogenated hydrocarbon such as methyl chloride, dichloromethane or chloroform, or acetone is preferred.

10 [0329]

In the aforementioned oxidation and cleavage reaction of the present invention, a precursor vinyl PHA, a permanganate salt and an acid may be introduced into a solvent at a time from the beginning and reacted
15 together, or they may be added to the reaction system one by one continuously or intermittently to be reacted. Or first a permanganate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a polyhydroxyalkanoate and an acid to the
20 reaction system, or first a polyhydroxyalkanoate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a permanganate and an acid to the reaction system. Further, first a polyhydroxyalkanoate and an acid are introduced into a
25 solvent and then a permanganate is added to the reaction system continuously or intermittently to be reacted, or first permanganate and an acid are

introduced into a solvent and then polyhydroxyalkanoate
is added to the reaction system continuously or
intermittently, or first a polyhydroxyalkanoate and a
permanganate are introduced into a solvent and then an
5 acid is added to the reaction system continuously and
intermittently to be reacted.

[0330]

A reaction temperature is selected generally
within a range from -40 to 40°C, preferably -10 to 30°C.
10 A reaction time depends on a stoichiometric ratio of
the unit represented by the chemical formula (1) and
permanganate salt and the reaction temperature, but is
generally selected within a range of 2 to 48 hours.

Also in the oxidation and cleavage reaction of the
15 present invention, in case R₂ in the unit represented
by the chemical formula (2) is a residue represented by
the chemical formula (11), a sulfide bond therein may
be converted into a sulfoxide or a sulfone.

[0331]

20 Next, there will be explained the producing method
of the precursor ester PHA of the present invention
employing, as a starting material, a polyhydroxy
alkanoate copolymer including a unit represented by the
chemical formula (32), and a unit represented by a
25 chemical formula (2) or a unit represented by a
chemical formula (3).

[0332]

A precursor ester PHA synthesized can provide the carboxyl PHA by hydrolysis in the presence of an acid or an alkali or hydrogenolysis including catalytic reduction of an ester bond portion shown in the chemical formula (48). Such method of hydrolysis in the presence of an acid or an alkali can be carried out by employing, in a water-miscible organic solvent such as methanol, ethanol, tetrahydrofuran, dioxane, dimethylformamide or dimethylsulfoxide, an aqueous solution or an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid; an organic acid such as trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid or methanesulfonic acid; an aqueous caustic alkali such as sodium hydroxide or potassium hydroxide; an aqueous solution or an alkali carbonate such as sodium carbonate or potassium carbonate; or an alcoholic solution of a metal alkoxide such as sodium methoxide or sodium ethoxide. The reaction temperature is selected ordinarily from 0 to 40°C, preferably from 0 to 30°C. The reaction period is ordinarily selected from 0.5 to 48 hours. However, a hydrolysis with an acid or an alkali may also cause a cleavage of an ester bonding of the main molecular chain, thereby resulting in a decrease in the molecular weight.

[0333]

Also the method of obtaining a carboxylic acid by

hydrogenolysis including catalytic reduction is carried out in the following manner. Catalytic reduction is carried out in a suitable solvent and within a temperature range from -20°C to the boiling point of the used solvent, preferably from 0 to 50°C, by reacting hydrogen under a normal pressure or an elevated pressure in the presence of a reducing catalyst. Examples of the usable solvent include water, methanol, ethanol, propanol, ethyl acetate, diethyl ether, tetrahydrofuran, dioxane, benzene, toluene, dimethylformamide and pyridine. In consideration of the solubility, tetrahydrofuran, toluene or dimethylformamide is particularly preferable. As the reducing catalyst, there can be employed palladium, platinum or rhodium either singly or held on a carrier, or Raney nickel. However, the catalytic reduction may also cause cleavage of an ester bonding of the main molecular chain to decrease the molecular weight.

[0334]

In the following, the present invention will be explained in more details by examples thereof. These examples represent examples of the optimum embodiments of the present invention, but the present invention is by no means limited by these examples.

[0335]

[Examples]

[Example 1]

0.5% of polypeptone (supplied by Wako Pure Chemical Co.), 6 mmol/L of 5-phenoxyvaleric acid, and 1 mmol/L of 10-undecenoic acid were dissolved in 200 ml of an aforementioned M9 culture medium, which was
5 placed in a 200 ml shaking flask, then sterilized in an autoclave and cooled to the room temperature. Then 2 ml of a culture liquid of *Pseudomonas cichorii* YN2, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours at 30°C, was
10 added to the prepared culture medium, and culture was conducted for 64 hours at 30°C. After the culture, the cells were collected by centrifugation, washed with methanol and dried. The dried cells, after weighing, were put in chloroform and stirred for 72 hours at 35°C
15 to extract a polymer. The chloroform extract was filtered, then concentrated on an evaporator, and a solid precipitate formed by an addition of cold methanol was collected and dried under a reduced pressure to obtain a desired polymer.

20 [0336]

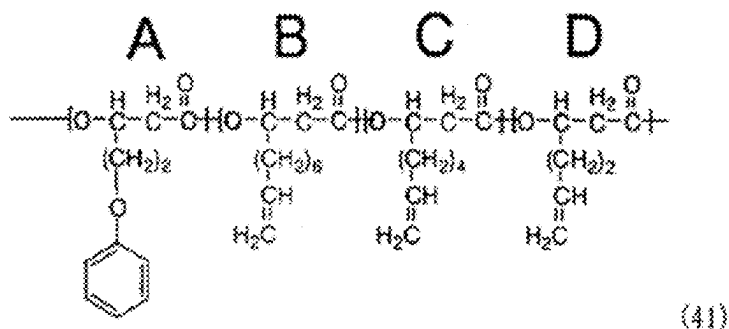
Structure of the obtained polymer was determined by ^1H -NMR (FT-NMR: Bruker DPX400; ^1H resonance frequency: 400 MHz; measured nucleus species: ^1H ; solvent: CDCl_3 ; reference: capillary-sealed TMS/ CDCl_3 ;
25 measurement temperature: room temperature).

Fig. 1 shows a ^1H -NMR spectrum of the obtained polymer. As a result, the obtained polymer was

confirmed being a polyhydroxy alkanoate copolymer including a unit represented by the following chemical formula (41) (A : B+C+D : others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) = 87 : 9 : 4). Also ^{13}C -NMR confirmed presence of the unit B which is a 3-hydroxy-10-undecenoic acid unit and both of the unit C which is a 3-hydroxy-8-nonenic acid unit and the unit D which is a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0337]

[Chemical Formula 232]



15 [0338]

The molecular weight of the obtained polymer was measured by gel permeation chromatography (GPC) (Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, molecular weight converted into polystyrene).

[0339]

The obtained polymer dry weight (PDW) was 0.19 g/L and the number-averaged molecular weight was 30,000.

[0340]

[Example 2]

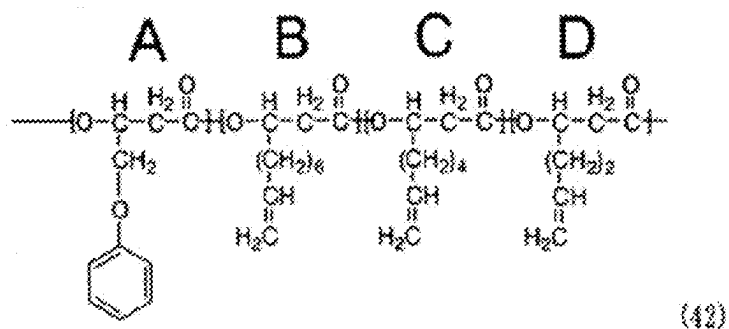
5 A desired polymer was obtained in the same manner as in Example 1, except that 5-phenoxyvaleric acid employed in Example 1 was changed to 4-phenoxybutyric acid.

[0341]

10 Structure of the obtained polymer was determined by ^1H -NMR and ^{13}C -NMR as in Example 1. Fig. 1 shows a ^1H -NMR spectrum of the obtained polymer. As a result, the obtained polymer was confirmed being a polyhydroxy alkanoate copolymer including units represented by the
15 following chemical formula (42) (A : B+C+D : others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) = 72 : 11 : 15). Also ^{13}C -NMR confirmed the presence of the unit B which is a 3-hydroxy-10-
20 undecenoic acid unit and both of the unit C which is a 3-hydroxy-8-nonenic acid unit and the unit D which is a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0342]

25 [Chemical Formula 233]



[0343]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

5 [0344]

The obtained polymer weighed (PDW) 0.05 g/L and a number-averaged molecular weight was 25,000.

[0345]

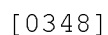
[Example 3]

10 A desired polymer was obtained in the same manner
as in Example 1, except that 5-phenoxyvaleric acid
employed in Example 1 was changed to 4-
cyclohexylbutyric acid.

[0346]

Structure of the obtained polymer obtained by ^1H -NMR and ^{13}C -NMR as in Example 1 was determined to confirm that the polyhydroxy alkanooate copolymer includes units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 89 : 11).

[Chemical Formula 234]



[0349]

15 [0350]

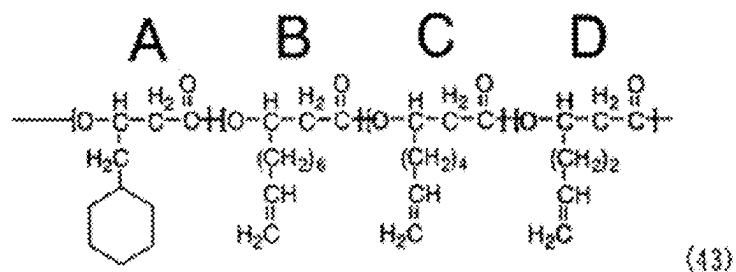
A desired polymer was obtained in the same manner as in Example 3, except that polypeptone employed in Example 3 was changed to yeast extract.

Structure of the obtained polymer was determined by ^1H -NMR and ^{13}C -NMR as in Example 1 to confirm the

polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 85 : 15). Also ^{13}C -NMR confirmed the presence of the unit B is a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

[0352]

[Chemical Formula 235]



[0353]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0354]

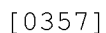
The obtained polymer weighed (PDW) 0.45 g/L and the number-averaged molecular weight was 132,000.

[0355]

[Example 5]

A polymer was obtained in the same manner as in

[Chemical Formula 236]



[0358]

The obtained polymer weighed (PDW) 0.41 g/L and the number-averaged molecular weight was 164,000.

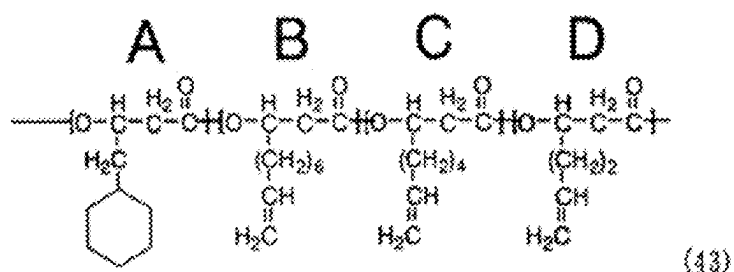
[0359]

[Example 6]

5 A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by *Pseudomonas cichorii* H45 and polypeptone was changed to sodium pyruvate. A structure determination of the obtained polymer was
10 conducted by ^1H -NMR and ^{13}C -NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-
15 hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 87 : 13). Also ^{13}C -NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit,
20 but the ratio of the units B, C and D was not determined.

[0360]

[Chemical Formula 237]



[0361]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

5 [0362]

The weight of the obtained polymer (PDW) was 0.28 g/L and the number-averaged molecular weight was 156,000.

[0363]

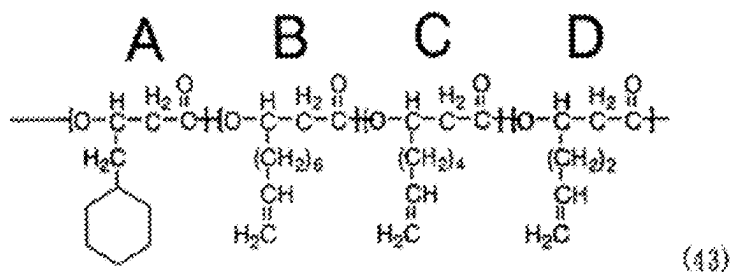
10 [Example 7]

A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by *Pseudomonas jessenii* P161 and polypeptone was changed to sodium glutamate. Structure determination of the obtained polymer was conducted by ^1H -NMR and ^{13}C -NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) : B+C+D = 88 : 12). Also ^{13}C -NMR confirmed the presence of the unit B being

a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenoic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was not determined.

5 [0364]

[Chemical formula 238]



[0365]

The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0366]

The weight of the obtained polymer (PDW) was 0.38 g/L and the number-averaged molecular weight of 145,000.

[0367]

15 [Example 8]

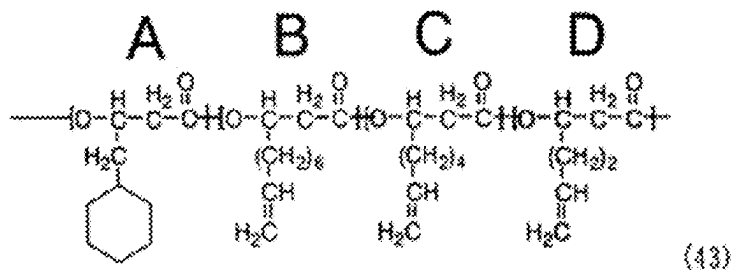
A polymer was obtained in the same manner as in Example 3, except that the strain YN2 employed in Example 3 was replaced by *Pseudomonas jessenii* P161 and 0.5% polypeptone was changed to 0.1% of nonanic acid.

20 The structure determination of the obtained polymer was conducted by ¹H-NMR and ¹³C-NMR as in Example 1 to confirm the polymer being a polyhydroxy alkanoate

copolymer including units represented by the following chemical formula (43) (A+others (linear 3-hydroxyalkanoic acid with 4 to 12 carbon atoms and 3-hydroxylalk-5-enoic acid with 10 or 12 carbon atoms) :
 5 B+C+D = 80 : 20). Also ^{13}C -NMR confirmed the presence of the unit B being a 3-hydroxy-10-undecenoic acid unit and both of the unit C being a 3-hydroxy-8-nonenic acid unit and the unit D being a 3-hydroxy-6-heptenoic acid unit, but the ratio of the units B, C and D was
 10 not determined.

[0368]

[Chemical Formula 239]



[0369]

15 The molecular weight of the obtained polymer was measured by GPC as in Example 1.

[0370]

The weight of the obtained polymer (PDW) was 0.18 g/L and the number-averaged molecular weight was
 20 132,000.

[0371]

[Example 9]

Twenty 200 ml shaking flasks were prepared, into which 0.5% of polypeptone (supplied by Wako Pure Chemical Co.), 6 mmol/L of 5-phenoxyvaleric acid, and 1 mmol/L of 10-undecenoic acid dissolved in 200 ml of an
5 aforementioned M9 culture medium was placed, then sterilized in an autoclave and cooled to the room temperature. Then 2 ml of a culture liquid of *Pseudomonas cichorii* YN2, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for
10 8 hours at 30°C, was added to each flask, and culture was conducted for 64 hours at 30°C. After the culture, all cells were collected by centrifugation, washed with methanol and dried. The dried cells, after weighing, were put in chloroform and stirred for 72 hours at 25°C
15 to extract a polymer. The chloroform extract was filtered, then concentrated on an evaporator, and a solid precipitate formed by an addition of cold methanol was collected and dried under a reduced pressure to obtain a desired polymer.

20 [0372]

The obtained PHA polymer weighed 1528 mg (dry weight) in the present example.

[0373]

The average molecular weight of the obtained PHA
25 was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a

result there were obtained a number-averaged molecular weight $M_n = 104000$ and a weight-averaged molecular weight $M_w = 231000$. The structure of the obtained polymer was determined by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ as in

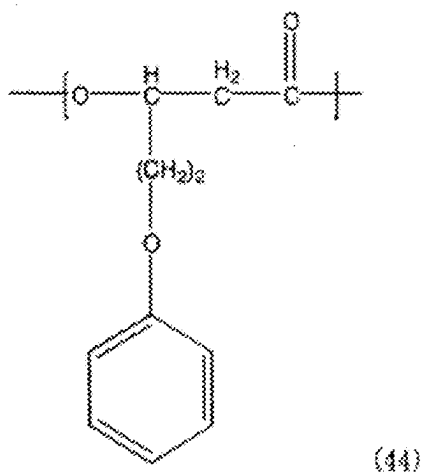
5 Example 1.

[0374]

As a result, confirmed was a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-phenoxyvaleric acid represented by the following
10 chemical formula (44), 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-nonenoic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenoic acid represented by a chemical formula (7).

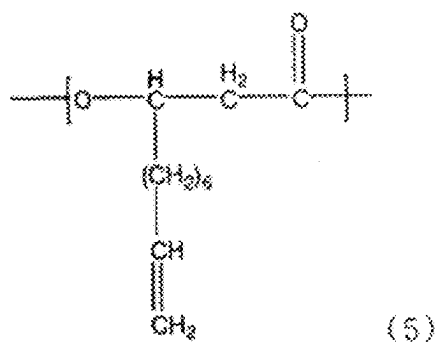
15 [0375]

[Chemical Formula 240]



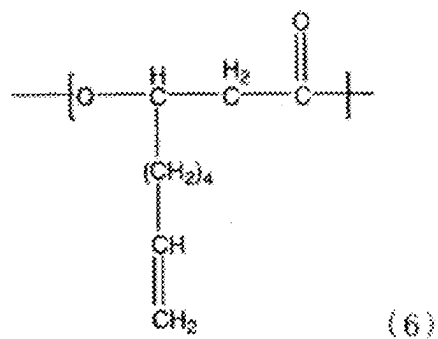
[0376]

[Chemical Formula 241]



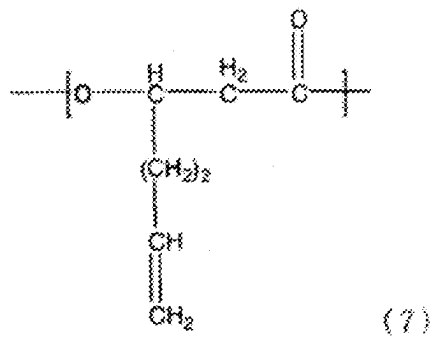
[0377]

[Chemical Formula 242]



5 [0378]

[Chemical Formula 243]



[0379]

The proportion of such units confirmed by $^1\text{H-NMR}$
 10 was: 69 mol% of 3-hydroxy-5-phenoxyvaleric acid, 23

mol% of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenoic acid and 3-hydroxy-6-heptenoic acid in total, and 8 mol% of others (linear 3-hydroxyalkanoic acids of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acids with 10 or 12 carbon atoms).
[0380]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction.
[0381]

10 303 mg of polyhydroxy alkanoate were charged in a 200-ml eggplant-shaped flask and were dissolved by adding 20 ml of dichloromethane. The solution was placed in an iced bath, and 3 ml of acetic acid and 300 mg of 18-crown-6-ether were added and agitated. Then,
15 in an iced bath, 241 mg of potassium permanganate were slowly added and an agitation was carried out for 20 hours at the room temperature. After the reaction, 50 ml of water and 500 mg of sodium bisulfite were added. Then the liquid was brought to pH = 1 by 1.0 N
20 hydrochloric acid. After dichloromethane in the mixed solvent was distilled off in an evaporator, a polymer in the solution was recovered. The polymer was recovered by washing with 100 ml of methanol and washing three times with 100 ml of purified water. A
25 drying under a reduced pressure provided 247 mg of the desired PHA.
[0382]

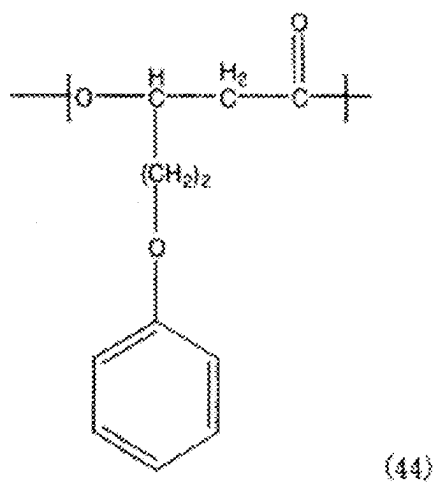
An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a
5 result there were obtained a number-averaged molecular weight $M_n = 29400$ and a weight-averaged molecular weight $M_w = 102800$.

[0383]

A structure determination of the obtained polymer
10 carried out by ^1H -NMR and ^{13}C -NMR as in Example 1 confirmed a polyhydroxy alkanoate copolymer including, as monomer units, 3-hydroxy-5-phenoxyvaleric acid represented by the following chemical formula (44), 3-hydroxy-9-carboxynonanoic acid represented by a
15 chemical formula (45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy-5-carboxyvaleric acid represented by a chemical formula (47).

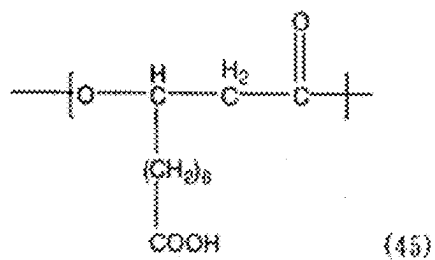
[0384]

20 [Chemical Formula 244]



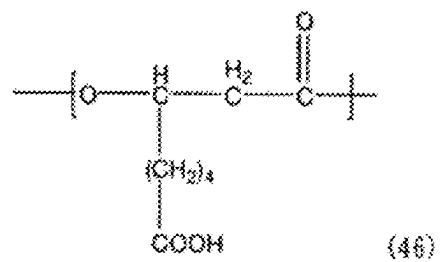
[0385]

[Chemical Formula 245]



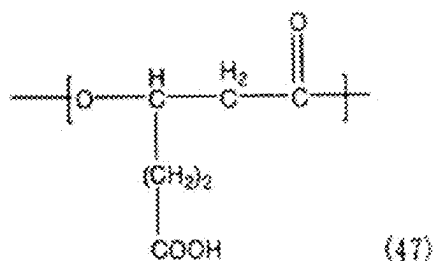
5 [0386]

[Chemical Formula 246]



[0387]

[Chemical Formula 247]



[0388]

Also a proportion of the units of the obtained PHA was calculated by a methylesterification, utilizing trimethylsilyldiazomethane, of a carboxyl group at an end of a side chain of the PHA.

[0389]

50 mg of the object PHA were charged in a 100-ml eggplant-shaped flask and were dissolved by adding 3.5 ml of chloroform and 0.7 ml of methanol. The solution was added with 2 ml of a 0.63 mol/L solution of trimethylsilyldiazomethane in hexane (supplied by Tokyo Kasei Co.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided 49 mg of PHA.

[0390]

NMR analysis as mentioned above confirmed a proportion of the units in which 3-hydroxy-5-phenoxyvaleric acid was present by 83 mol%, a sum of

three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-heptanoic acid and 3-hydroxy-5-valeric acid by 8 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 5 10 or 12 carbon atoms) by 9 mol%.

[0391]

[Example 10]

There were prepared twenty 500-ml shake flasks, and, in each, 0.5 wt.% of polypeptone (supplied by Wako
10 Pure Chemical Co.), 6 mmol/L of 4-cyclohexylbutyric acid, and 3 mmol/L of 10-undecenoic acid were dissolved in 200 ml of an aforementioned M9 culture medium, which was placed in a 500 ml shake flask, then sterilized in an autoclave and cooled to the room temperature. Then
15 2 ml of a culture liquid of *Pseudomonas cichorii* YN2 strain, shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours, was added to each prepared culture medium, and culture was conducted for 60 hours at 30°C. After the culture, the
20 culture liquids were united, and the cells were recovered by centrifuging, rinsed with methanol and dried. The dried cells, after weighing, were agitated with chloroform for 72 hours at 25°C to extract a polymer. The chloroform extract was filtered with a
25 0.45 μ m membrane filter, then concentrated in an evaporator, and the polymer was recovered by a reprecipitation in cold methanol. A desired polymer

was then obtained by drying under a reduced pressure.

[0392]

According to a weighing of the obtained polymer,
1433 mg (dry weight) of PHA were obtained in the
5 present example.

[0393]

An average molecular weight of the obtained PHA
was measured by gel permeation chromatography (GPC:
Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H,
10 solvent: chloroform, converted to polystyrene). As a
result there were obtained a number-averaged molecular
weight $M_n = 143000$ and a weight-averaged molecular
weight $M_w = 458000$.

[0394]

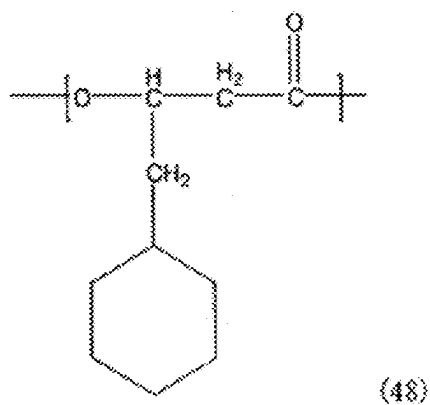
15 A structure of the obtained PHA was determined by
a NMR analysis as in Example 1.

[0395]

As a result, there was confirmed a polyhydroxy
alkanoate copolymer including, as monomer units, 3-
20 hydroxy-5-cyclohexylbutyric acid represented by the
following chemical formula (48), 3-hydroxy-10-
undecenoic acid represented by a chemical formula (5),
3-hydroxy-8-nonenoic acid represented by a chemical
formula (6) and 3-hydroxy-6-heptenoic acid represented
25 by a chemical formula (7).

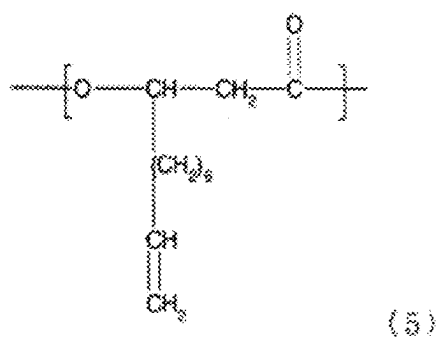
[0396]

[Chemical Formula 248]



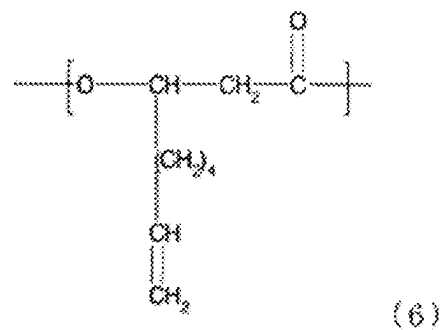
[0397]

[Chemical Formula 249]



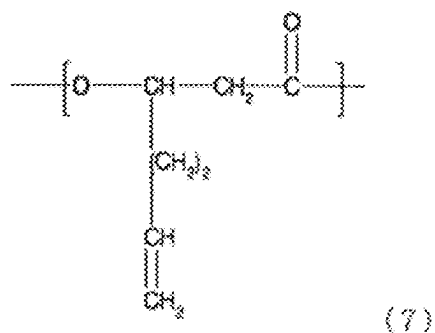
5 [0398]

[Chemical Formula 250]



[0399]

[Chemical Formula 251]



[0400]

Also a proportion of such units was confirmed by $^1\text{H-NMR}$ spectrum, where a sum of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenic acid and 3-hydroxy-6-heptenoic acid was present by 37 mol%, and 3-hydroxy-4-cyclohexylbutyric acid and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 63 mol%.

[0401]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction.

[0402]

301 mg of polyhydroxy alkanoate were charged in a 200-ml eggplant-shaped flask and were dissolved by adding 20 ml of dichloromethane. The solution was placed in an iced bath, and 3 ml of acetic acid and 541 mg of 18-crown-6-ether were added and agitated. Then, in an iced bath, 430 mg of potassium permanganate were slowly added and an agitation was carried out for 20 hours at the room temperature. After the reaction, 50

ml of water and 1000 mg of sodium bisulfite were added.
Then the liquid was brought to pH = 1 by 1.0 N
hydrochloric acid. After dichloromethane in the mixed
solvent was distilled off in an evaporator, a polymer
5 in the solution was recovered. The polymer was
recovered by washing with 100 ml of methanol and
washing three times with 100 ml of purified water. A
drying under a reduced pressure provided 184 mg of the
desired PHA.

10 [0403]

An average molecular weight of the obtained PHA
was measured by gel permeation chromatography (GPC:
Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H,
solvent: chloroform, converted to polystyrene). As a
15 result there were obtained a number-averaged molecular
weight $M_n = 111800$ and a weight-averaged molecular
weight $M_w = 272800$.

[0404]

For specifying the structure of the obtained PHA,
20 a NMR analysis was carried out under conditions same as
in Example 1.

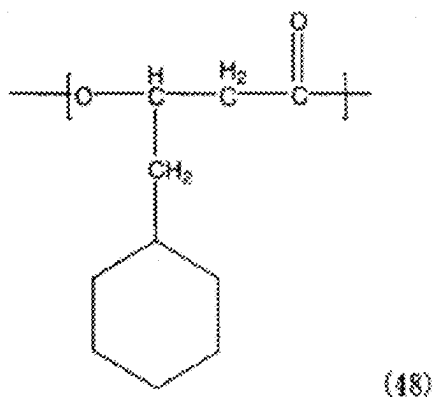
[0405]

As a result, there was confirmed a polyhydroxy
alkanoate copolymer including, as monomer units, 3-
25 hydroxy-4-cyclohexylvaleric acid represented by the
following chemical formula (48), 3-hydroxy-9-
carboxynonanoic acid represented by a chemical formula

(45), 3-hydroxy-7-carboxyheptanoic acid represented by a chemical formula (46) and 3-hydroxy-5-carboxyvaleric acid represented by a chemical formula (47).

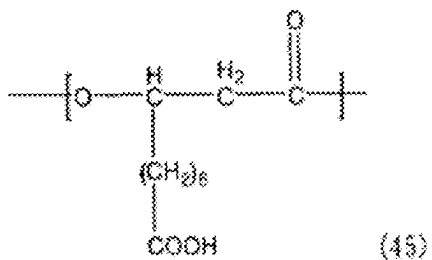
[0406]

5 [Chemical Formula 252]



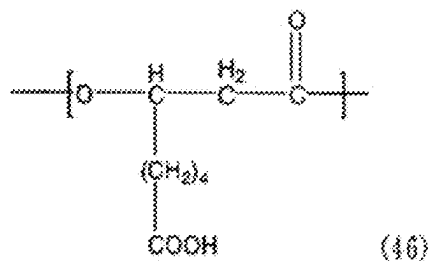
[0407]

[Chemical Formula 253]



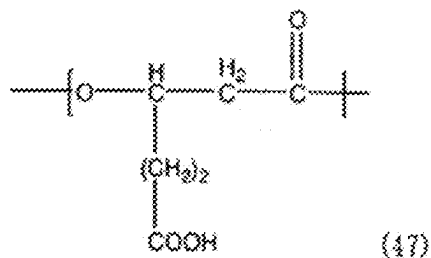
10 [0408]

[Chemical Formula 254]



[0409]

[Chemical Formula 255]



5 [0410]

Also a proportion of the units of the obtained PHA was calculated by a methylesterification, utilizing trimethylsilyldiazomethane, of a carboxyl group at an end of a side chain of the PHA.

10 [0411]

30 mg of the object PHA were charged in a 100-ml eggplant-shaped flask and were dissolved by adding 2.1 ml of chloroform and 0.4 ml of methanol. The solution was added with 0.9 ml of a 0.63 mol/L solution of
 15 trimethylsilyldiazomethane in hexane (supplied by Tokyo Kasei Co.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided 31 mg of PHA.

[0412]

5 A NMR analysis was carried out as mentioned above. As a result, ¹H-NMR spectrum confirmed a proportion of the units in which a sum of three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-carboxyheptanoic acid and 3-hydroxy-5-carboxyvaleric acid was present by 9
10 mol%, and 3-hydroxy-4-cyclohexyl butyric acid and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 91 mol%.

[0413]

15 [Example 11]

 There were prepared three 2000-ml shake flasks, and, in each, 0.5 wt.% of polypeptone (supplied by Wako Pure Chemical Co.), 4.8 mmol/L of 5-(phenylsulfanyl)valeric acid, and 2 mmol/L of 10-
20 undecenoic acid were dissolved in 1000 ml of an aforementioned M9 culture medium, which was placed in a 2000 ml shake flask, then sterilized in an autoclave and cooled to the room temperature. Then 10 ml of a culture liquid of *Pseudomonas cichorii* YN2 strain,
25 shake cultured in advance in an M9 culture medium containing 0.5% of polypeptone for 8 hours, was added to each prepared culture medium, and culture was

conducted for 38 hours at 30°C. After the culture, the culture liquids were united, and the cells were recovered by centrifuging, rinsed with methanol and dried. The dried cells, after weighing, were agitated
5 with chloroform for 25 hours at 35°C to extract a polymer. The chloroform extract was filtered with a 0.45 µm membrane filter, then concentrated in an evaporator, and the polymer was recovered by a reprecipitation in cold methanol. A desired polymer
10 was then obtained by drying under a reduced pressure.
[0414]

According to a weighing of the obtained polymer, 1934 mg (dry weight) of PHA were obtained in the present example.
15 [0415]

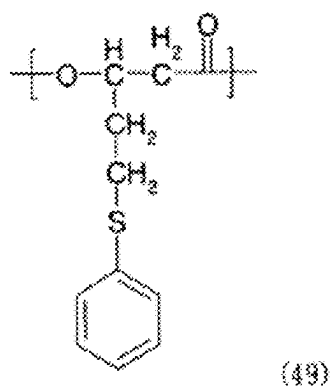
An average molecular weight of the obtained PHA was measured by gel permeation chromatography (GPC: Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H, solvent: chloroform, converted to polystyrene). As a
20 result there were obtained a number-averaged molecular weight $M_n = 430000$ and a weight-averaged molecular weight $M_w = 150000$.
[0416]

A structure of the obtained PHA was determined by
25 a NMR analysis as in Example 1. An obtained ^1H -NMR spectrum is shown in Fig. 3.
[0417]

As a result, there was confirmed a polyhydroxy
 alkanate copolymer including, as monomer units, 3-
 hydroxy-5-(phenylsulfanyl)valeric acid represented by
 the following chemical formula (49), 3-hydroxy-10-
 5 undecenoic acid represented by a chemical formula (5),
 3-hydroxy-8-nonenoic acid represented by a chemical
 formula (6) and 3-hydroxy-6-heptenoic acid represented
 by a chemical formula (7).

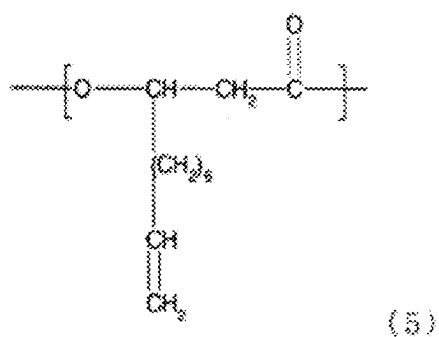
[0418]

10 [Chemical Formula 256]



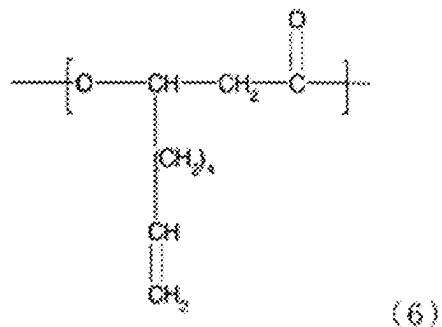
[0419]

[Chemical Formula 257]



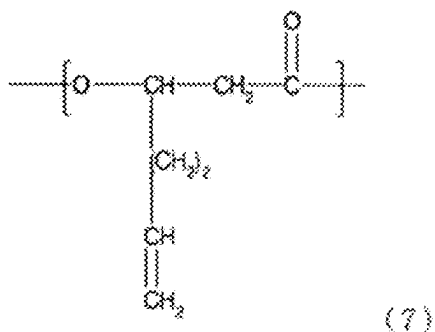
15 [0420]

[Chemical Formula 258]



[0421]

[Chemical Formula 259]



5

[0422]

Also a proportion of such units was confirmed by ¹H-NMR spectrum, where 3-hydroxy-5-(phenylsulfanyl)valeric acid was present by 78 mol%, a sum of three units of 3-hydroxy-10-undecenoic acid, 3-hydroxy-8-nonenic acid and 3-hydroxy-6-heptenoic acid by 19 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic acid with 10 or 12 carbon atoms) by 3 mol%.

15 [0423]

The polyhydroxy alkanoate thus obtained was utilized in the following reaction. 302 mg of

polyhydroxy alkanoate were charged in a 200-ml
eggplant-shaped flask and were dissolved by adding 20
ml of dichloromethane. The solution was placed in an
iced bath, and 3 ml of acetic acid and 1154 mg of 18-
5 crown-6-ether were added and agitated. Then, in an
iced bath, 917 mg of potassium permanganate were slowly
added and an agitation was carried out for 19 hours at
the room temperature. After the reaction, 50 ml of
water and 3010 mg of sodium bisulfite were added. Then
10 the liquid was brought to pH = 1 by 1.0 N hydrochloric
acid. After dichloromethane in the mixed solvent was
distilled off in an evaporator, a polymer in the
solution was recovered. The polymer was recovered by
washing with 100 ml of methanol and washing three times
15 with 100 ml of purified water. A drying under a
reduced pressure provided 311 mg of the desired PHA.
[0424]

An average molecular weight of the obtained PHA
was measured by gel permeation chromatography (GPC:
20 Toso HLC-8220 GPC, column: Toso TSK-GEL Super HM-H,
solvent: chloroform, converted to polystyrene). As a
result there were obtained a number-averaged molecular
weight $M_n = 62000$ and a weight-averaged molecular
weight $M_w = 260000$.
25 [0425]

For specifying the structure of the obtained PHA,
a NMR analysis was carried out under conditions same as

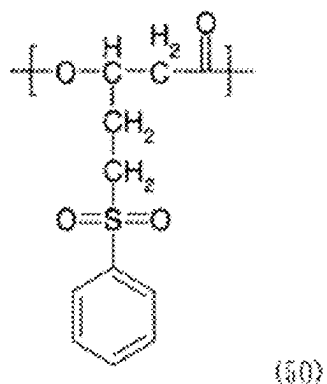
in Example 1. An obtained ^1H -NMR spectrum is shown in Fig. 4.

[0426]

As a result, there was confirmed a polyhydroxy
5 alkanooate copolymer including, as monomer units, 3-
hydroxy-5-(phenylsulfonyl)valeric acid represented by
the following chemical formula (50), 3-hydroxy-9-
carboxynonanoic acid represented by a chemical formula
(45), 3-hydroxy-7-carboxyheptanoic acid represented by
10 a chemical formula (46) and 3-hydroxy-5-carboxyvaleric
acid represented by a chemical formula (47).

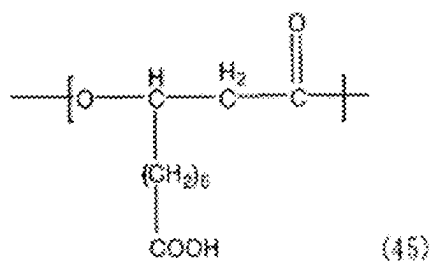
[0427]

[Chemical Formula 260]



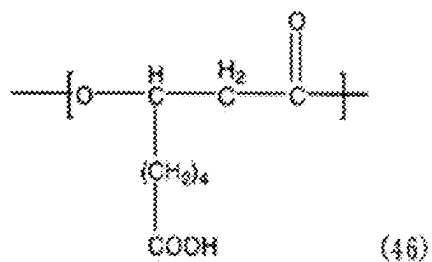
15 [0428]

[Chemical Formula 261]



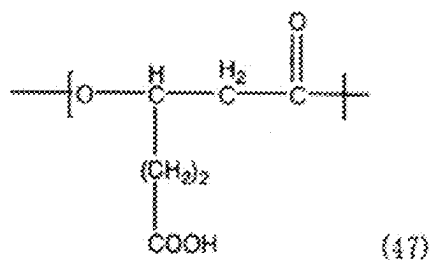
[0429]

[Chemical Formula 262]



5 [0430]

[Chemical Formula 263]



[0431]

Also a proportion of the units of the obtained PHA
 10 was calculated by a methylesterification, utilizing
 trimethylsilyldiazomethane, of a carboxyl group at an
 end of a side chain of the PHA.

[0432]

30 mg of the object PHA were charged in a 100-ml

eggplant-shaped flask and were dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. The solution was added with 0.5 ml of a 2 mol/L solution of trimethylsilyldiazomethane in hexane (supplied by
5 Aldrich Inc.) and was agitated for 30 minutes at the room temperature. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was recovered by washing with 50 ml of methanol. A drying under a reduced pressure provided
10 31 mg of PHA.

[0433]

A NMR analysis was carried out as in Example 1. As a result, ¹H-NMR spectrum confirmed a proportion of the units in which 3-hydroxy-5-(phenylsulfonyl)valeric acid
15 was present by 89 mol%, a sum of three units of 3-hydroxy-9-carboxynonanoic acid, 3-hydroxy-7-carboxyheptanoic acid and 3-hydroxy-5-carboxyvaleric acid by 8 mol%, and others (linear 3-hydroxyalkanoic acid of 4 to 12 carbon atoms and 3-hydroxyalk-5-enoic
20 acid with 10 or 12 carbon atoms) by 3 mol%.

[0434]

[Effect of the Invention]

The method of the present invention provides a novel polyhydroxy alkanoate copolymer including a unit
25 having a vinyl group in a side chain and a unit including a residue having any of a phenyl structure, a thienyl structure, and a cyclohexyl structure in the

side chain simultaneously.

[0435]

The present invention further provides a method for producing PHA such that PHA can be produced at a high yield, the unit ratio of the side chain having a vinyl group can be controlled, and physical properties of PHA thus produced can be regulated. The present invention provides a polyhydroxy alkanoate copolymer including a monomer unit having a carboxyl group at the end of a side chain and unusual PHA having on the side chain thereof a substituent other than a linear alkyl group, such as a phenyl structure, a thienyl structure or a cyclohexyl structure, and a producing method therefor.

[Brief Description of the Drawings]

[Fig. 1] A ^1H -NMR spectrum of a polyester obtained in Example 1.

[Fig. 2] A ^1H -NMR spectrum of a polyester obtained in Example 2.

[Fig. 3] A ^1H -NMR spectrum of a polyhydroxy alkanoate copolymer obtained in Example 11, and including 3-hydroxy-5-(phenylsulfanyl)valeric acid represented by a chemical formula (49), a 3-hydroxy-10-undecenoic acid represented by a chemical formula (5), 3-hydroxy-8-nonenic acid represented by a chemical formula (6) and 3-hydroxy-6-heptenic acid represented by a chemical formula (7).

[Fig. 4] A ^1H -NMR spectrum of a polyhydroxy
alkanoate copolymer obtained in Example 11, and
including 3-hydroxy-5-(phenylsulfonyl)valeric acid
represented by a chemical formula (50), a 3-hydroxy-9-
5 carboxynonanoic acid represented by a chemical formula
(45), 3-hydroxy-7-carboxyheptanoic acid represented by
a chemical formula (46) and 3-hydroxy--5-carboxyvaleric
acid represented by a chemical formula (47).

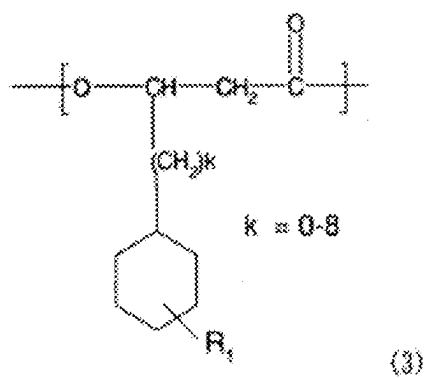
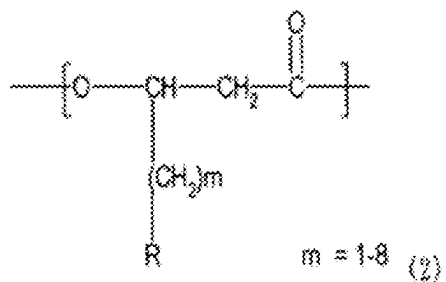
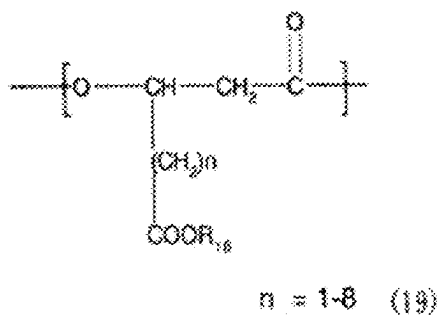
[Name of the Document] Abstract

[Abstract]

[Problem(s)] It is to provide PHA having an active
group and a production method therefor, such that PHA
5 can be produced by a microorganism at a high yield, the
unit ratio of the active group can be controlled, and
its physical properties can be freely regulated not to
limit its application as a polymer.

[Means for Solving the Problem(s)] The invention
10 provides a PHA copolymer including at least a 3-
hydroxy- ω -carboxyalkanoic acid represented by a formula
(19) and simultaneously at least a unit represented by
a formula (2) or a formula (3) in a molecule, a
precursor PHA copolymer having a corresponding vinyl
15 group or a corresponding alkoxycarbonyl group, a
biosynthesis method thereof by microorganisms, and a
method of producing a desired PHA copolymer from the
precursor PHA copolymer:

[Chemical Formula 1]

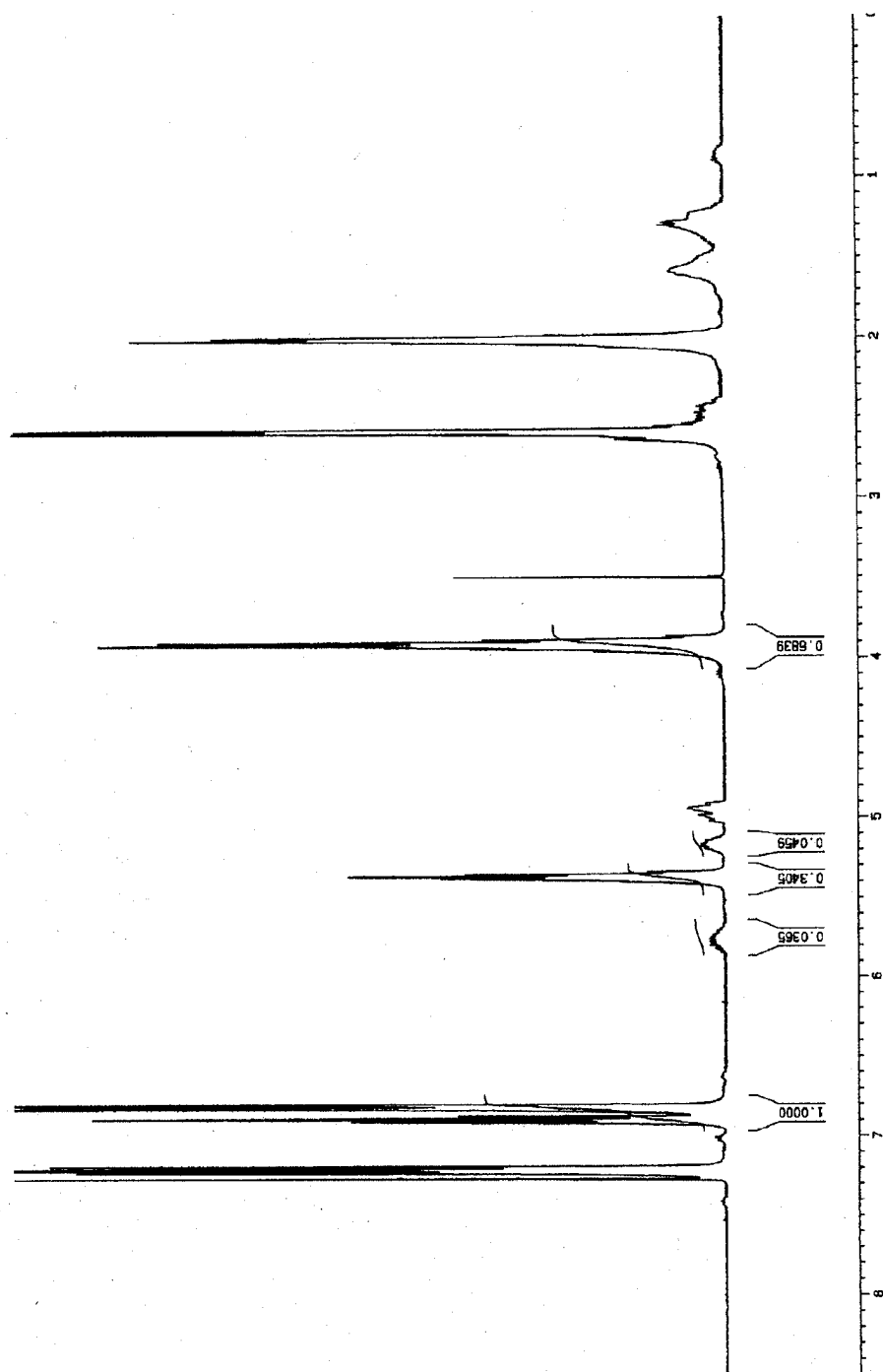


(wherein k, m, n are integers; R₁₈ represents H, Na, K, or; R₁ represents a substituent on a cyclohexyl group and represents H, CN, NO₂, a halogen atom, CH₃, C₂H₅,
5 C₃H₇, CF₃, C₂F₅, or C₃F₇; R includes a residue including a phenyl structure or a thienyl structure; these being independent for each unit).

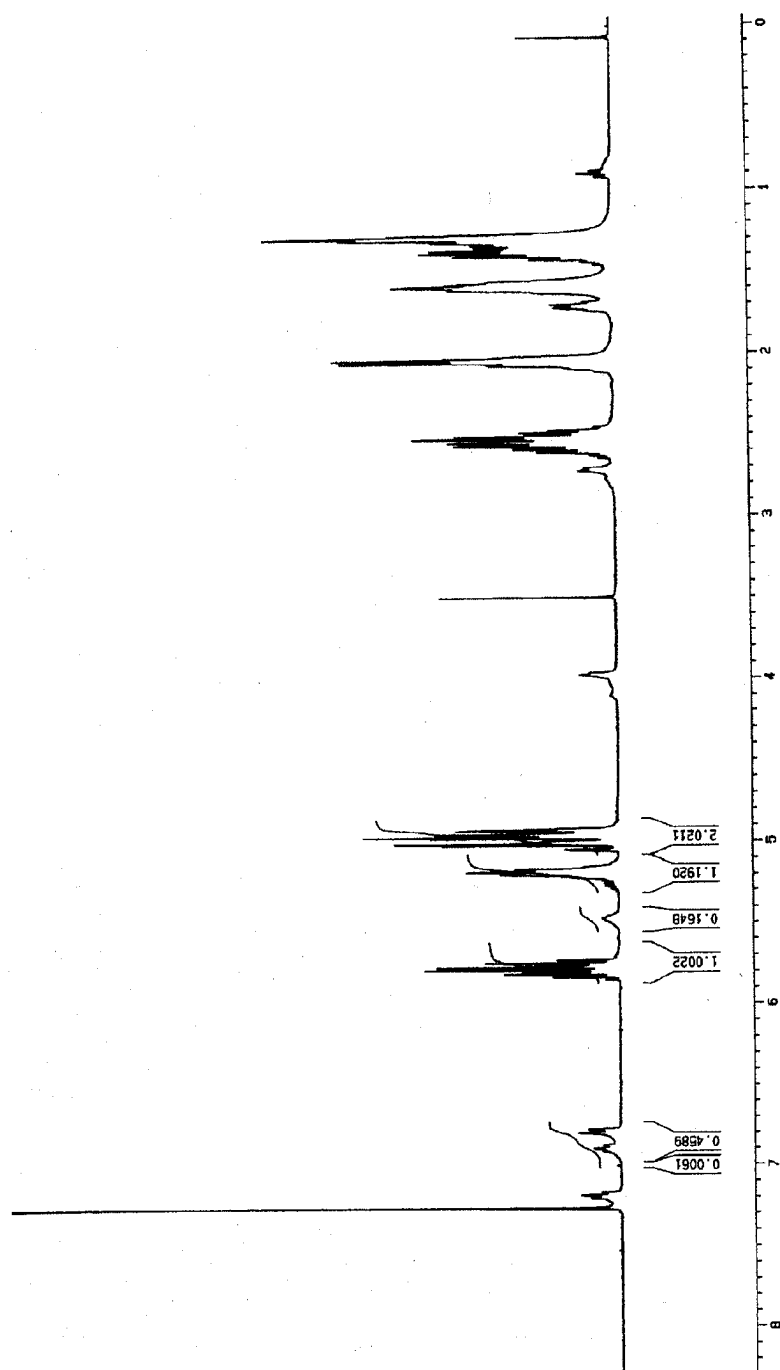
[Elected Drawing] None

【書類名】 図面

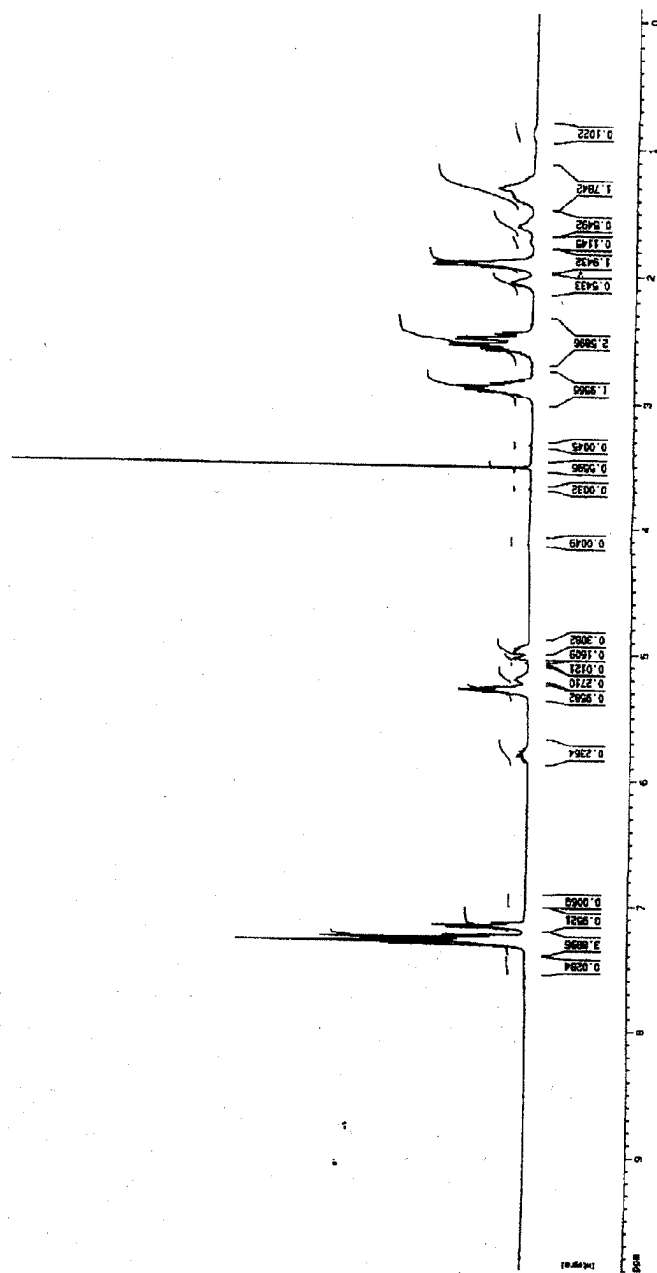
【図1】



【図2】



【図3】



【図4】

